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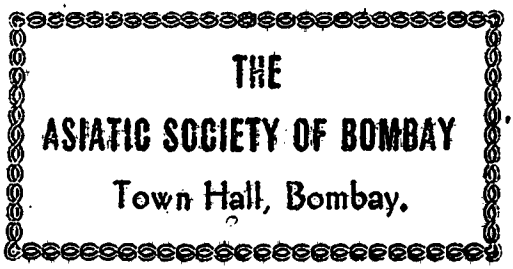

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AN

ESSAY ON PHLOGISTON,

AND THE

CONSTITUTION OF ACIDS.

A NEW EDITION.

By R. KIRWAN, Esq.

Member of the Academies of Stockholm, Upsal, Dijon, Dublin, Philadelphia, Manchester, &c.

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ac

To which are added,

NOTES,

Exhibiting and defending the Antiphlogistic Theory; and annexed to the French Edition of this Work; by Messrs. de Morveau, Lavoisier, de la Place, Monge, Berthollet, and de Fourcroy:

TRANSLATED INTO ENGLISH.

cc h 2

WITH

ADDITIONAL REMARKS AND REPLIES,

By the AUTHOR.

LONDON:

PRINTED FOR J. JOHNSON, No 72,

ST. PAUL'S CHURCH-YARD.

1789.

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THE

ENGLISH TRANSLATOR's

PREFACE.

THE ſame natural cauſe which impels the human mind to form general inferences from particular events, is the ground of every theoretic ſyſtem. In the conſtruction of ſuch a ſyſtem, or general hypotheſis, by which the facts in any experimental ſcience are arranged and referred to univerſal laws, the facility muſt be greater the fewer the facts: becauſe there are many ſuppoſitions which will ſerve to account for a few facts; but the true theory muſt be diſcovered before an adequate ſolution of a greater variety of events can be obtained. The hiſtory of ſcience ſhews, however, that it is by no means eaſy to acquire that ſtrength of mind which is neceſſary to enable the enquirer after truth to give up his former train of ideas, and examine with candour and impartiality the conſequences ſuggeſted by phenomena, viewed

in a new light. The paſſions too often interfere. A deſire of victory, or of diſtinction, frequently produces an obſtinate adherence to the tenets we have maintained; and even where this does not happen, there is a degree of indolence in avoiding new and laborious inveſtigations, and an impatience of doubt, from which perhaps no mind is free, that induce us to adapt the facts to our hypotheſes, rather than employ that time and exertion, which would probably exhibit the true laws of natural appearances. Theſe are difficulties which alike oppoſe both innovation and improvement; and would greatly retard the progreſs of ſcience, if ſimilar motives did not give activity to the promulgators of new doctrines, and produce controverſies which are always of advantage to truth. The opponents in this method of inveſtigation, mutually enlighten each other; and whether perſonal conviction be produced or not, yet ſociety at large is highly benefited by their obſervations and diſcoveries. The received doctrines either become eſtabliſhed with greater firmneſs, or are compelled to give place to others which are better founded.

In the work before us, the public is preſented with moſt of the facts and deductions

relating to a controverſy, on a ſubject of the moſt extenſive importance. The parts of all bodies tend to approach each other, and this tendency would end in abſolute repoſe, if it were not counteracted by ſome other energies. In the unlimited regions of ſpace, as far as obſervation can reach, or imaginary conjecture extend itſelf, we perceive that a force of projection is oppoſed to that attraction, which would otherwiſe bring numberleſs worlds into one immenſe maſs. In our planetary ſyſtem we find, that the revolutions produced by the compoſition of the gravitating and projectile forces, cauſe certain regular changes of heat or temperature on the globe we inhabit, and doubtleſs on the others which revolve round the ſun. The ſcience of chemiſtry, though confeſſedly in its infancy, informs us that this heat, or cauſe of temperature, whatever it may be, is the great opponent to the coheſive attraction, which, if not thus oppoſed, would prevent every change among the parts of bodies. When heat is communicated to bodies, they aſſume the various forms of expanded ſolidity, fluidity, and elaſticity. In the two laſt ſtates, they combine and exhibit thoſe various diſpoſitions to unite or ſeparate, which have been referred to ſpecific attractions,

called the chemical affinities. During theſe proceſſes the temperatures are changed in conſequence of certain effects, which are all referable to the general and wonderful proceſs, known by the name of combuſtion. It is therefore a leading conſideration, and, as it were, the very ſoul of chemiſtry, to determine what happens when bodies undergo combuſtion. Whether ſuch bodies as increaſe their temperature until their total decompoſition, when they are heated with the acceſs of air, do contain any common principle of inflammability; or whether they ſimply poſſeſs a power of combining ſtrongly and rapidly with a part of the atmoſphere? is the great queſtion agitated in the following ſheets; by a philoſopher of the firſt eminence amongſt us, who maintains the exiſtence of the phlogiſton: while the contrary opinion is ſupported by men whoſe ſucceſsful labours, in this department of ſcience, have entitled them to the higheſt conſideration, from all its cultivators, and from every friend to ſociety.

I need not enlarge upon the advantages that muſt reſult from the compreſſion of this controverſy into one ſmall volume, by ſuch men; neither need I, nor can I with propriety, make

make any obſervations in this place upon their deductions. My own part, as tranſlator, has been performed with a degree of diligence and attention, which will be properly valued by thoſe who know that this taſk, ſubordinate as it is, requires an intimate knowledge of the ſubject and no ſmall care, before the tranſlation can be offered to men of ſcience, as a ſubſtitute for the original. This I can venture to do with confidence, and flatter myſelf that it contains no errors; or, if there be any, that they are very few.

Though I think it proper to avoid any interference in the arguments of the reſpectable authors of this publication, and have taken that liberty, by adding a note, in one ſingle inſtance only; yet I ſhall not ſcruple to offer a few remarks concerning the limits of error in chemical experiments; with the hope that they will have ſome effect upon the future reſearches of ſuch chemiſts as have not paid ſufficient attention to this circumſtance.

When chemiſts reaſon upon the ſubjects and products which paſs under their obſervation, they chiefly enquire into their nature and qualities, but take it for granted that the

quantities are accurate. In this laſt particular they would be juſtifiable, if the quantities or weights were always entered from actual experiments, without reduction or other computation. It happens, however, moſt commonly, in the determination of weights, which is half the buſineſs of a chemiſt, that on account of the admiſſion of elements of ſpecific gravities, carried to too many places of figures, or in conſequence of reductions of vulgar fractions to decimals, or ſometimes from actual noting of weights to a degree of minuteneſs which experiment cannot juſtify, we find the reſults to exhibit an unwarrantable pretenſion to accuracy. To counteract this, I muſt obſerve, that,

1. Such beams as have been uſed by the moſt accurate operators, and are ſpoken of as being extraordinarily good, do not in general weigh accurately beyond four places of figures*: and conſequently all weights

* Of theſe it will be ſufficient to mention Muſchenbrock's balance; Cours de Phyſique, II. 246: Bolton's two balances; Philoſophical Tranſactions, LXVI. 509: Whitehurſt's balance, ibid. p. 576: Mr. Alchorne's ſtrong balance; ibid. LXXVII. 205: Monſ. Tillet's balance; Acad. Par. 1767, and M. Lavoiſier's ſmall beam; Traité Elem. de Chimie, p. 334.

ſet

ſet down to more places, are deceptions either of inadvertence or intention.

2. If we admit of the pretended accuracy of beams, which are ſaid to have weighed to five and ſix places of figures*; yet they could not be thus uſed in the ordinary courſe of experiments, becauſe their motion cannot but be extremely ſlow: not to mention that the proportional accuracy of all beams is relative to one particular weight or load only, and diminiſhes if that load be altered either way.

3. The error of weighing any elaſtic fluid is at leaſt thirty times as great, in proportion to the whole, as in common weighing. For the glaſs globe and apparatus made uſe of, muſt be extremely light indeed, if it be not thirty times as heavy as the included air.

* Of theſe I find only Mr. Read's ſtrong beam; Phil. Tranſ. LXVI. 511: Dr. Fordyce's beam, by Ramſden; ibid. LXXVII: M. Lavoiſier's ſtrong beam; Traité de Chimie, 334: and the Royal Society's balance, by Ramſden. The three firſt weigh to five, and the laſt to ſix places of figures. The point of ſuſpenſion cannot, even in theory, when at beſt, move through ſo large a ſpace as five hundredths of an inch, during the firſt minute, in this laſt mentioned balance, though it ſeems to be, in all reſpects, the beſt I have ever ſeen or heard of.

Hence

Hence if a beam weighs to five places of figures in common, it will not weigh an elaſtic fluid to a greater accuracy than three, and an eſtimate or gueſs figure. And the error of determining the abſolute weights of given quantities of air will be rendered greater, by the uncertain allowances for temperature and preſſure, and the various quantities of moiſture they may contain, according to their manner of reception, and time of expoſure to water, which cannot be avoided in experiments on a large ſcale. For theſe reaſons it may be doubted whether the ſpecific gravities of elaſtic fluids can, in general, be depended on as far as three places of figures.

I will not extend this Preface, by invidiouſly pointing out how far theſe circumſtances, obvious as they are, have been overlooked by ſeveral experimental philoſophers, who deſerve and poſſeſs a very high degree of eſtimation. But as a reference to weights in the experiments of Mr. Lavoiſier is made to conſtitute a great part of the arguments adduced to prove the compoſition of water, and its decompoſition, I think it proper (highly as I eſteem his talents) to take notice that his writings abound with ſpecific gravities of elaſtic fluids, carried to five places of figures, which are ſo far from being given

as

as eſtimate numbers, that they are uſed as elements in reſults, carried to ſix, ſeven, and even eight places of figures. If it be denied that theſe reſults are pretended to be true in the laſt figures, I muſt beg leave to obſerve, that theſe long rows of figures, which in ſome inſtances extend to a thouſand times the nicety of experiment, ſerve only to exhibit a parade which true ſcience has no need of: and, more than this, that when the real degree of accuracy in experiments is thus hidden from our contemplation, we are ſomewhat diſpoſed to doubt whether the *exactitude ſcrupuleuſe** of the experiments be indeed ſuch as to render the proofs *de l'ordre demonſtratif*.

When we reflect on the grand experiment of the gun-barrel, and conſider that it requires the accurate determination of the weight of a gun-barrel of ten or twelve pounds, both before and after the ignition; of an enormous bulk of inflammable air received over water; and alſo of vital air employed in the recompoſition—we cannot help wiſhing to know the limits of error, and how far they may affect the inferences. This appears to be an object worthy of the attention of the French Academicians. Every

* See p. 65 of the original, or 59 of this tranſlation.

friend

friend to ſcience muſt own his obligations to their inſtructive labours; and I ſhould feel no ſmall degree of regret, if I ſuppoſed the preſent obſervations could be attributed to any deſire of depreciating their merits, or indeed to any motive but an attachment to truth.

WILLIAM NICHOLSON.

LONDON, *May* 30, 1789.

THE

THE

FRENCH TRANSLATOR's

PREFACE.

THE ſtudy of chemiſtry becomes daily more general, and its advances appear to be more particularly rapid ſince a philoſopher, well known for the ſcrupulous attention with which he makes his experiments, and the philoſophical ſpirit which has directed his obſervations, has formed a new theory, in which nothing is admitted but eſtabliſhed truths. This has been readily adopted by moſt of the philoſophers of France: indeed it was difficult to avoid obſerving that a doctrine which explains all the facts of chemiſtry without any ſuppoſition, which follows the progreſs of nature ſtep by ſtep, and whoſe reſults always agree with the moſt rigorous calculation, muſt be preferable to another theory, which accounts for the experiments

of

of the ſame nature, in no other way than by continual ſuppoſitions, and which in ſome inſtances contradicts itſelf.

Such, however, was the ſyſtem imagined by Stahl, concerning the exiſtence and properties of phlogiſton, and which Macquer, Bergman, and Scheele, have followed by modifying it.

Whatever difficulties this theory might preſent, it could not be expected that the diſciples of theſe juſtly celebrated men would abandon it without reſiſtance. They accordingly employed, at firſt, every exertion of their abilities in palliating the contradictions; afterwards they inſiſted on all the experiments which might ſeem to favour it; and laſtly, ſome among them, while they retained the word Phlogiſton, concluded by giving it another ſignification. This is particularly the caſe with Mr. Kirwan. Among the philoſophers who have not yet adopted the new doctrine, he is certainly one of thoſe who is the moſt capable of producing uncertainty in the minds of ſuch perſons as decide by authority. His acquaintance with every part of natural philoſophy; the diſcoveries with which he has

has enriched the ſciences, and even the ingenious modifications he has introduced into the theory of phlogiſton; all contribute to give weight to his opinions. If the French chemiſts, whom he has oppoſed, ſhould deſtroy his objections, will they not perhaps have a right to conclude that there are not any other ſolid objections to be made? It is principally from this laſt conſideration that a tranſlation of his Eſſay on Phlogiſton was determined upon: care has been taken to render it as literal as the difference of the languages would allow, and to expreſs the ideas of Mr. Kirwan in the cleareſt and moſt preciſe manner: the extreme accuracy which ſcientific matter demands, renders it neceſſary to uſe the greateſt ſtrictneſs in the choice of expreſſions.

But this labour would not have ſufficiently advanced the revolution which is preparing in chemiſtry, and the uſeful purpoſe intended would not have been accompliſhed, if there had not been joined to the tranſlation of Mr. Kirwan's work, ſuch obſervations as it might give riſe to. Some of the philoſophers who do not believe in the exiſtence of phlogiſton, have taken care to draw them out. They cannot be ſuſpected of partiality. Penetrated with

with an equal eſteem for Mr. Kirwan, they earneſtly deſire his concurrence; and moſt of them have formerly adopted his opinions.

Mr. de Morveau, whom Mr. Kirwan not long ſince reckoned in the number of phlogiſtians, has repeated with the greateſt care, in a viſit he made to Paris laſt year, thoſe experiments which ſerve as the baſis of the new doctrine: that of the combuſtion of charcoal in oxigenous gas or vital air, and its entire transformation into carbonic acid gas: that of the combuſtion of ſpirit of wine, whoſe reſult affords a weight of water ſuperior to that of the liquor employed. He has diſcuſſed, with ſevere logic, the proofs of the formation of water by the combuſtion of hydrogenous or inflammable gas, and oxigenous gas, as well as thoſe of its decompoſition, and the ſeparation of the two elements which compoſe it. Theſe experiments, which are explained in the moſt ſimple and natural manner, according to the new doctrine, appeared to him more than ſufficient to juſtify his abandoning the hypotheſis of phlogiſton.

Mr. Berthollet had already, ſome years before, renounced the ancient theory; he was invincibly

invincibly led to the antiphlogiſtian doctrine, by experiments made upon the formation of acids, by his own diſcoveries concerning the oxigenated muriatic acid, and on the decompoſition of ammoniac or volatile alkali, and by a great number of other facts, of which the phlogiſtians can give only forced explanations.

Moſt of the French philoſophers have followed theſe zealous defenders of the new doctrine. Mr. de la Place, Mr. Monge, and Mr. Meuſnier in ſeveral memoirs; Mr. de Fourcroy in his lectures at Paris; Mr. Chaptal at Montpelier; Mr. le Febvre de Gineau, poſſeſſor of the new chair of philoſophy, which his Majeſty has founded at the Royal College; have baniſhed phlogiſton from their writings and their lectures: experience has ſhewn them, by the ſucceſs of their works, and their numerous audiences, that the public opinion was not againſt them. Moſt of theſe philoſophers have contributed to the obſervations placed at the end of the ſeveral ſections of the preſent tranſlation of Mr. Kirwan's work. They have not made it a point, in their replies, to diſcuſs each individual objection; they were deſirous of avoiding details fatiguing to the reader, and

which ſimple notes did not permit. They have confined themſelves to prove a ſmall number of ſimple and fundamental truths relating to each diviſion of the ſubject, from which an explanation of all the phenomena of chemiſtry is naturally derived.

The Tranſlator has added only a few notes of no great conſequence.

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INTRODUCTION.

THOUGH combuſtion, together with ſeveral of the moſt ſtriking phenomena of chymiſtry, and particularly of metallurgy, were known to mankind from the earlieſt ages, yet it does not appear that any general concluſions were deduced from them, or any theory attempted before the 9th century; in the dark interval between that and the 13th, the qualities of bodies began to be claſſed both by phyſicians and alchymiſts, and, according to the general ſpirit of the philoſophy of thoſe times, attributed to thoſe peculiar ſubſtances that ſeemed to poſſeſs them in the moſt eminent degree. In this diſtribution of qualities, that of inflammability was aſſigned to *ſulphur*, and in a looſe ſenſe, this was erected into one of the five chymical principles; but about the middle of the laſt century, the Carteſian philoſophy then prevailing,

vailing, vague qualities were every where proſcribed, and more exact and preciſe notions eagerly ſought. Beccher, a German metallurgiſt of great ſagacity, and perfectly acquainted with all the chymical facts then extant, which were much more numerous than is commonly believed, perceiving that ſulphur, properly ſo called, did not exiſt in animal or vegetable ſubſtances though inflammable, firſt aſſerted, that ſulphur was not the principle of inflammability, but that this quality reſided in a ſubſtance common to ſulphur, and to vegetable, animal, and various mineral bodies: this ſubſtance he ſuppoſed to be of a *dry* nature, and therefore called it an earth, on which, by way of diſtinction, he beſtowed the name of *Phlogiſton*.

This doctrine, ſome years after, was adopted, improved, and extended by the celebrated Stahl, and a theory formed which ſoon produced a variety of curious and uſeful diſcoveries: moſt chymical phænomena were ſo happily illuſtrated and regularly connected by this theory, that ſince the year 1736, it was univerſally received all over Europe.

It muſt be owned, however, that this doctrine reſted on the ſuppoſition that inflammable bodies contain ſome ſubſtance which uninflammable bodies do not; nor have chymiſts, until within theſe few years, been able to afford any proof that this ſuppoſition was well found-

ed, as they were never able to exhibit this ſubſtance ſingly and by itſelf, for which inability they accounted by ſaying, that on quitting one body it always united to another. With this reaſoning moſt chymiſts acquieſced, and the rather, as they found it impoſſible to ſubſtitute a better theory in its place. Even the weight which many metallic ſubſtances were known to gain when they were ſaid to have loſt their phlogiſton, did not for a long time ſhake the credit of this favourite hypotheſis: it was held by ſome, that this increaſe of weight was owing to the acceſſion of igneous particles; by others, that phlogiſton was a principle of levity. Rey, in the laſt century, aſcribed it to its true cauſe, the abſorption of air, but on ſuch weak grounds, that he is as little intitled to the honour of a diſcoverer, as a ſucceſsful dreamer to that of a prophet: nor can I with juſtice aſcribe this honour to Dr. Hales, though he firſt extracted air from minium; as he imputed the increaſe of weight not only to the air, but alſo to ſulphur, which he imagined it abſorbed from the fire. Mr. Lavoiſier was undoubtedly the firſt who proved, by direct and exact experiments, that the weight which metals gain by calcination correſponds with that of the air which they abſorb; he was alſo the firſt who publiſhed that the atmoſphere conſiſts of two diſtinct fluids, the one fit for the purpoſes of reſpiration and combuſtion, which he therefore calls *vital* or *pure* air;

air; the other unfit for either purpoſe, and thence called *foul* or mephitic air; and that in the atmoſphere the proportion of the firſt was to that of the laſt nearly as 1 to 4; he alſo proved after Dr. Crawford, that pure air (a ſubſtance which Dr. Prieſtley firſt diſcovered, and called dephlogiſticated air) contained more fire than any other air, and that during combuſtion, it gave out this fire in the form of heat and light.

On theſe grounds Mr. Lavoiſier reverſed the ancient hypotheſis; inſtead of ſuppoſing that inflammable bodies contained a peculiar ſubſtance which uninflammable bodies do not; he ſuppoſes that inflammable bodies are ſuch as have in a certain degree of heat a ſtrong affinity to pure air; and he proved by experiment, that the remains of theſe bodies after inflammation, and metallic bodies after calcination, contain a ſubſtance which they did not contain before; and hence he at firſt modeſtly propoſed his doubts, whether the ſuppoſition of ſuch a ſubſtance, as the chymiſts called phlogiſton, were not entirely ſuperfluous: But as the nature of aerial fluids yearly received a fuller illuſtration from the numerous and ingenious experiments of Dr. Prieſtley, it was inferred from many of them, as well as from an attentive conſideration of various chymical phenomena, that inflammable air, before its extrication from the bodies in which it exiſts in a concrete ſtate, was the

very

very ſubſtance to which all the characters and properties of the phlogiſton of the ancient chymiſts actually belonged, and conſequently that it was no longer to be regarded as a mere hypothetical ſubſtance, ſince it could be exhibited in an aerial form in as great a degree of purity as any other air.

This opinion ſeems to have met the approbation of the moſt diſtinguiſhed philoſophers, both at home and abroad*; nor can I ſee what Mr. Lavoiſier could reply, before the important diſcovery of the compoſition of water made by Mr. Cavendiſh. This furniſhed him with a new and unexpected ſource from which he could derive the inflammable air, extricated in various operations on inflammable and metallic bodies. However, in adopting this explanation, Mr. Lavoiſier departs from thoſe laws of philoſophic reaſoning with the breach of which he before reproached his opponents: that water is a compound ſubſtance, has been proved by direct experiment, but that it is decompoſed in any chymical operation, is a mere gratuitous ſuppoſition; nor can he ſay that it is an equal chance whether the inflammable air extricated during the ſolution

* Dr. Prieſtley, Mr. Bewly, Mr. Bergman, Mr. Morveau, De La Metherie, Chaptal, Crell, Wiegleb, Weſtrumb, Hermſtadt, Kaerſten, &c.

of a metal proceeds from the decompoſition of water, or from the decompoſition of the metal; for the metals that principally afford it, as iron and zinc, are by themſelves, and in the total abſence of water, perfectly inflammable, and therefore ſhould be deemed to poſſeſs the ſame principle of inflammability as vegetable and animal ſubſtances, whoſe inflammability, without any controverſy, is attributed to the preſence of inflammable air, whereas water can be inflamed in no circumſtances whatſoever.

The ſubſtances which Mr. Lavoiſier allows to contain the inflammable principle diſtinct from water, are oils, reſins, ſpirit of wine *, and volatile alkalis †, and conſequently all vegetable and animal ſubſtances; even charcoal he allowed at firſt to be an *unknown modification* of the inflammable principle, though at preſent he ſeems to think otherwiſe; if he allows it to contain the inflammable principle conſolidated by unknown means, as ice is a modification of water, we ſhall hardly diſpute it, though in reality, it, together with that, contains alſo fixed air, as will appear in the ſequel ‡.

The controverſy is therefore at preſent confined to a few points, namely, whether the *inflammable principle* be found in what are called

* Mem. Par. 1781, p. 491, 492.

† 29 Roz. p. 175.

‡ See p. 10. This reference is annexed by the French tranſlator.

phlo-

phlogiſticated acids, vegetable acids, fixed air, ſulphur, phoſphorus, ſugar, charcoal, and metals.

Limited as this controverſy appears to be to a ſmall number of bodies, it is nevertheleſs of great importance, if an exact arrangement of our ideas, and a diſtinct and true view of the operations of nature, be of any importance. The bodies above-mentioned are the ſubject of many, and the inſtruments of almoſt all chymical operations: without a knowledge of their compoſition, and a clear perception of their mode of action, it will be impoſſible to form even an approximation to a ſolid theory of this ſcience; the daily accumulation of facts will only increaſe perplexity and confuſion, and if any uſeful diſcovery be made, it will be the mere reſult of chance.

Many ſtrong prejudices, I am well aware, favour the new opinion (which I ſhall take the liberty of calling the *Antiphlogiſtic* hypotheſis, and its ſupporters *Antiphlogiſtians*, not by way of obloquy, but to prevent circumlocution): it has been advanced in an enlightened age and country, it is recommendable by its ſimplicity, and it owes its origin to a philoſopher of great eminence, who was the firſt that introduced an almoſt mathematical preciſion into experimental philoſophy; but the old ſyſtem preſents alſo many ſtrong prejudices in its favour; it originated,

nated, it is true, in a leſs enlightened age, but it originated in a country in which chymical knowledge then was, and ſtill is, further advanced than in any other part of Europe. It is to Germany that all modern nations muſt reſort, to improve in mineralogy and metallurgy, as the ancients did to Greece to improve in oratory. By the Germans, as alſo by the Swedes, the old doctrine has gradually been improved and refined, and their attachment to it is ſtill unſhaken. We muſt not be deluded by a falſe ſhew of ſimplicity; when all is well conſidered, the ancient doctrine will be found the more uniform of the two; in this, pure air is never ſaid to unite to any ſubſtance, but to the principle of inflammability with which it is evidently ſeen to unite in the deflagration of inflammable air; in the modern, without being an acid, or affording any ſign of ſalinity, the principal prerogative of acid ſubſtances, that of uniting to almoſt all bodies, is aſſigned to it.

But prejudices of every kind ſhould certainly be laid aſide in all ſcientifical inquiries; truth, if it can *evidently* be traced, or if not, the *internal probability* of any principle, ſhould be the only motive of our attachment to it. Now, that doctrine muſt be accounted the leaſt probable which fails oftenеſt in explaining the phænomena, is more arbitrary in its application, and leſs countenanced by the

the general rules of philoſophic reaſoning; that this is the caſe of the antiphlogiſtic hypotheſis, I flatter myſelf will appear after an attentive peruſal of the following ſections.

NOTE

NOTE

OF

MR. LAVOISIER

UPON THE

INTRODUCTION.

AS it does not appear that Mr. Kirwan has formed perfect ideas of the doctrine which he diſtinguiſhes by the name of Antiphlogiſtic, I find it neceſſary, before I enter into any diſcuſſion, to preſent in this place a ſhort account of the principles upon which it is founded: and in order to avoid a repetition of work already done, I ſhall have recourſe principally to the report which Meſſ. Berthollet, de Fourcroy, and myſelf, read to the Academy, concerning two Memoirs of Meſſ. Haſſenfratz and Adet. This report is printed at page 288 of the Method of Chemical Nomenclature, which we have propoſed. It is not exactly ſuited to the preſent exigency, becauſe we did not at that time propoſe to write an anſwer to Mr. Kirwan; but

but as we have determined to tranſcribe it, we do not think it allowable to make any alteration, but have conſidered it as a duty to adhere minutely to the text. The following are the words we made uſe of.

" If a ſolid body, for example ice, be taken " and heated, it will be converted into water; " and this water expoſed to a heat of 80 de- " grees, will aſſume the form of vapour or " gas. The ſame obſervation may be made " upon almoſt all bodies in nature. They " are ſolid, liquid, or aeriform, according to " the degree of heat they are expoſed to *. " Modern philoſophy has even diſcovered " means to determine with accuracy the ratio " of the quantities of heat neceſſary to con- " vert certain ſolid bodies into liquids, and " liquids into aeriform fluids †.

" In the enunciation of theſe facts, mak- " ing uſe of the new nomenclature which " we have adopted, we ſhall ſay that gas or " an aeriform fluid is a combination of *caloric* " with a given ſubſtance; and, in fact, when- " ever gas is formed, there is an abſorption " of heat, and, reciprocally, whenever gas is

* See the Memoir on the combination of the matter of fire with evaporable fluids, and upon the formation of elaſtic aeriform fluids; inſerted in the Memoirs of the Academy of Sciences for the year 1777, page 420. Conſult likewiſe page 595 et ſeq. of the ſame Vol.

† See the Memoir on Heat, in the Memoirs of the Academy of Sciences for the year 1780, page 355.

" con-

" converted into the ſolid or fluid ſtate, the
" portion of caloric neceſſary to conſtitute
" the ſtate of gas appears again, and is ſet
" at liberty *. This enunciation is rigorouſly
" true, whatever idea may be attached to the
" word Caloric, whether it be conſidered as
" a very ſubtle elaſtic fluid, or whether it be
" regarded merely as a modification †.

" We do not deny the exiſtence of caloric
" in ſolid bodies ‡; to pretend the contrary,
" would be to act againſt evidence. But we
" affirm that the ſame body contains more
" caloric in the liquid than in the ſolid ſtate,
" and ſtill more when it is converted into the
" aeriform ſtate. We are not yet acquainted
" with any exception to this general prin-
" ciple.

" It is therefore neceſſary to diſtinguiſh in
" every ſpecies of gas, the caloric which per-
" forms the office of a ſolvent, and the ſub-
" ſtance which is united to it, and ſerves as
" a baſe. Vital air therefore has its baſe, and
" it is to this baſe that we give the name of
" *oxigene*. In the ſame manner we diſtin-
" guiſh the baſe of inflammable gas, and

* Mem. Acad. 1777, page 424.

† " We do not in this place make any diſtinction be-
" tween caloric and light, though ſuch a diſtinction is very
" neceſſary; but we have here avoided it, becauſe we were
" apprehenſive of interrupting the chain of reaſoning by too
" long a digreſſion."

‡ Mem. Acad. 1783, page 524 et ſeq.

" call

" call it by the name of *hydrogene*. We do " not therefore affirm, that vital air combines " with metals to form metallic calces, becauſe " this manner of enunciating would not be " ſufficiently accurate: but we ſay, when a " metal is heated to a certain temperature, and " when its particles are ſeparated from each " other to a certain diſtance by heat, and their " attraction to each other is ſufficiently dimi- " niſhed, it becomes capable of decompoſing " vital air, from which it ſeizes the baſe, " namely *oxigene*, and ſets the other prin- " ciple, namely the *caloric*, at liberty. This " explanation of what paſſes during the cal- " cination, is not an hypotheſis, but the reſult " of facts. It is upwards of twelve years " ſince the proofs have been laid by one of " us, before the eyes of the Academy, and " have been verified by a numerous commiſ- " ſion *. It was then eſtabliſhed, that when " the calcination of metals is effected either " beneath an inverted glaſs veſſel, or in cloſed " veſſels containing known quantities of air, " the air itſelf is decompoſed, and the weight " of the metal becomes augmented by a " quantity accurately equal to that of the air " abſorbed. It has ſince been found that when " the operation was performed in very pure " vital air, the whole might be abſorbed;

* See the Opuſcules Chymiques of M. Lavoiſier, chap. 5 et 6, part 2.

" that

" that when the proceſs was made in veſſels
" hermetically ſealed, the calcination was
" limited by the quantity of air contained in
" the veſſels, but that the veſſel itſelf neither
" gained nor loſt weight during the operation *.
" Laſtly, it has been obſerved, that the
" more rapid the calcination of the metal, the
" more ſpeedy was the diſengagement of the
" caloric; and that the calcination of iron,
" for example, became a true combuſtion
" when performed in vital air.

" There is likewiſe a total abſorption of
" vital air, or rather of the *oxigene* which
" forms its baſe, in the combuſtion of phoſ-
" phorus; and the weight of the phoſphoric
" acid obtained is found to be rigorouſly equal
" to the weight of the phoſphorus, added to
" that of the vital air employed in its com-
" buſtion †. The ſame agreement of weights
" is obſerved in the combuſtion of inflam-
" mable gas and vital air, in the combuſtion
" of charcoal, &c ‡. In theſe operations, the
" caloric and the light, which maintained the
" *oxigene* in a ſtate of expanſion, are ſet at li-
" berty, with this remarkable circumſtance,
" however, that there is more caloric diſen-
" gaged in the combuſtion of inflammable

* Mem. Acad. 1747, [1777] page 351 et ſeq.

† See the Opuſcules Chymiques of Mr. Lavoiſier, chap. 9, page 329. and the Mem. of the Acad. for the year 1777. page 65. et ſeq.

‡ Acad. of Sciences 1781, pages 448 et 468.

" gas,

" gas, than in that of phoſphorus, becauſe
" the two airs afford it; whereas, on the con-
" trary, there is a leſs quantity diſengaged in
" the combuſtion of charcoal, becauſe the re-
" ſult of this combuſtion being the carbonic
" acid, or fixed air, this laſt requires a quan-
" tity of caloric to maintain it in the aeriform
" ſtate.

" No ſuppoſition enters into theſe expla-
" nations; the whole is proved by weight
" and meaſure. Why, therefore, need we
" have recourſe to an hypothetical principle,
" the exiſtence of which is ever ſuppoſed, and
" has never been proved; which in one caſe
" muſt be conſidered as heavy, and in another
" as void of weight, and to which, in ſome
" caſes, it is neceſſary even to ſuppoſe a ne-
" gative weight; a ſubſtance which in ſome
" inſtances paſſes through the veſſels, and in
" others is retained by them; a being which
" its maintainers dare not rigorouſly define,
" becauſe its merit and its convenience conſiſt
" even in the uncertainty of the definitions
" which are given of it?

" There is no doubt of the value of the
" fact obſerved by Stahl, that the property of
" combuſtibility may be transferred from one
" body to another, according to the certain
" laws and affinities. But at preſent, when
" we know that the property of burning is
" nothing elſe but the property which certain
" ſubſtances poſſeſs of decompoſing vital air

" by

" by the great affinity they have for the ..
" ginous principle, the general obſervation of
" Stahl is reduced to this ſimple enunciation,
" *that a body ceaſes to be combuſtible when its*
" *affinity for the oxigene is ſatisfied, or when it*
" *is ſaturated with that principle; but that it*
" *becomes again combuſtible when the oxigene*
" *has been taken from it by another body which*
" *has a ſtronger affinity with that principle.*

" One of the points of the modern doc-
" trine, which appears the moſt firmly eſta-
" bliſhed, is the formation, the decompo-
" ſition, and recompoſition of water. And
" how can it be poſſible to doubt this, when
" we ſee by burning together 15 grains of
" inflammable gas and 85 of vital air, the
" product is exactly 100 grains of water,
" from which we can, by the way of decom-
" poſition, again recover the ſame two prin-
" ciples in the ſame proportions *. If any
" doubts be entertained of a truth eſtabliſhed
" by ſuch ſimple and palpable experiments,
" there can be no certainty in natural philo-
" ſophy. It might with equal propriety be
" queſtioned whether vitriolated tartar be
" really compoſed of vitriolic acid and fixed
" alkali, ſal ammoniac of marine acid and
" volatile alkali, &c. &c. For the proofs
" which we have of the compoſition of theſe

* Mem. Acad. 1781, page 269 et ſeq. 468 et ſeq.

" ſalts

" ſalts are of the ſame kind, and are not
" more ſtrict than thoſe which eſtabliſh the
" compoſition of water.

" Nothing perhaps can better prove the
" inſufficiency of the ancient theory, than
" the forced explanations which have been
" attempted to be given of theſe experi-
" ments.

" The water, ſay they, which is obtained,
" exiſted in the two airs or gaſes which ſerv-
" ed for the combuſtion *: but 100 grains
" of air cannot contain 100 grains of water;
" otherwiſe it would be neceſſary to affirm
" that inflammable gas is water, and that
" vital air is water, and that theſe two aeriform
" fluids are the ſame thing; which is con-
" trary to evidence, ſince it is a principle,
" that two bodies, which have very different
" properties, cannot be one and the ſame
" thing.

" Beſides this, there is another kind of ex-
" periments, which overthrows the whole of
" this ſyſtem of explanation; namely, the
" revivification of metallic calces in inflam-
" mable gas by the burning glaſs. If a
" pint, that is to ſay 2 grains of inflammable
" gas †, be paſſed under a bell or jar filled
" with mercury, and its mouth plunged

* See the method of chemical nomenclature, pages 249 et 250.

† By Dr. Prieſtley's experiments.

" in the ſame fluid, and if a metallic calx be
" then introduced, and this calx be heated
" by the focus of a burning glaſs, the in-
" flammable gas will be totally abſorbed; at
" the ſame time that the metal is revived,
" and a conſiderable quantity of water is de-
" poſited, as well on the ſides of the glaſs as
" upon the ſurface of the mercury. The quan-
" tity of water obtained in this operation has
" not yet been determined by accurate expe-
" riments; but it at leaſt proved that it
" greatly exceeds the weight of the inflam-
" mable gas made uſe of. It cannot therefore
" have been contained in that gas, and it
" would be abſurd to ſuppoſe that 2 grains of
" inflammable gas could contain 8 or 10
" grains of water, or even a larger quantity in
" ſolution.

" In addition to this we may obſerve, that
" it is not merely by the way of recompoſi-
" tion, that the diſcovery that water is a
" compound ſubſtance, and the determination
" of the nature of the principles which enter
" into its combination, have been aſcertained;
" for they are again found by the way of
" analyſis or decompoſition; ſo that, on this
" ſubject, the moſt complete chemical proof
" has been obtained. Nothing more is ne-
" ceſſary than to preſent to the water a body
" which has a ſtrong affinity, either with the
" hydrogene or baſe of inflammable gas, or
" with the oxigene or baſe of vital air, to ef-
" fect

" fect the ſeparation of the conſtituent parts
" of water. By this treatment it is decom-
" poſed, and that principle of the water
" which does not enter into the new combi-
" nation, unites with the *caloric*, and is ex-
" hibited in the form of gas *. The great
" phænomena of the nutrition and growth of
" animals and vegetables, the various kinds
" of fermentation, &c. afford numerous ex-
" amples of theſe decompoſitions.

" Mr. Cavendiſh and Mr. Kirwan do not
" entirely agree with us reſpecting the nature
" of the conſtituent principles of water; they
" have formed different hypotheſes concerning
" the nature and compoſition of inflammable
" gas and vital air. For our part, as we
" have made it a law to draw no concluſions
" beyond the warrant of facts, we are content
" to affirm, that water is a compound of the
" baſe of vital air, and that of inflammable
" gas, of oxigene and hydrogene; and while
" we keep within theſe limits, we are aſſured
" of committing no error.

" We proceed to the theory of acidification,
" if we may with propriety give the name of
" theory to a truth of fact and obſerva-
" tion which by its generality may be re-
" garded as a conſtant law of nature. We
" We have not yet ſucceeded in decompoſing
" and recompoſing all the acids; but we are

* Mem. Acad. 1781, page 468.

" aſſured at leaſt, that the oxigene is a prin-
" ciple common and neceſſary to the forma-
" tion of all thoſe whoſe compoſition we are
" acquainted with. Thus it is a matter of
" fact ſtrictly proved by experiment, that
" ſulphur cannot be converted into the ſul-
" phuric or vitriolic acid, but ſo far as it is
" combined with once and an half its weight
" of the baſe of vital air or oxigene; that in
" the ſame manner phoſphorus does not be-
" come phoſphoric acid, nor charcoal the
" carbonic acid or fixed air, but by combin-
" ing with 2½ parts of oxigene, &c. Thus
" far it may be ſeen the new doctrine of aci-
" dification is ſimply the expoſition of fact.
" But when, from theſe particular facts, the
" general induction is made, that oxigene is a
" principle common to all acids, the conſe-
" quence is founded on analogy, and here it
" is that the theory commences. Experi-
" ments which daily become more numerous,
" afford an increaſing probability to this theo-
" ry, and we do not think that this is the
" leaſt important part of the new doctrine *."

Nothing can be more eaſy, after this ſhort explanation of the antiphlogiſtic doctrine, than to form an idea of what I underſtand by inflammability. An inflammable body is no-

* See the Opuſcules Phyſiques et Chimiques of Mr. Lavoiſier, chap. 9. Mem. Acad. for the year 1776, page 671; year 1777, page 65 & 504; year 1778, page 555.

thing

thing elſe but a body which has the property of decompoſing vital air, and taking the baſe from the caloric and light, that is to ſay the oxigene which was united to them. When this decompoſition of the air is rapid, and as it were inſtantaneous, there is an appearance of flame, heat, and light; when, on the contrary, the decompoſition is very ſlow, and quietly made, the heat and light are ſcarcely perceptible.

If therefore we attach to the word Inflammability the idea of diſengagement of caloric and light, ſuch as takes place in the phænomena of combuſtion and calcination, we muſt conclude, that vital air or oxigynous gas is the inflammable body moſt eminently, ſince it is principally and almoſt entirely from this ſubſtance that the caloric and light are diſengaged.

Mr. Kirwan pretends that the queſtion is at preſent reduced to determine, whether the inflammable principle be found in phlogiſticated acids, vegetable acids, fixed air, ſulphur, phoſphorus, charcoal, and metals? Yes, doubtleſs, theſe ſubſtances have the property of inflaming and burning, when they are heated in the air; that is to ſay, they have the property of decompoſing the air or oxigenous gas, from which they ſeize the baſe and ſeparate the caloric. But it is not neceſſary, in the explanation of this effect, to ſuppoſe, with Mr. Kirwan, that there exiſts in theſe ſubſtances a prin-

ciple common to them all; that they all contain the baſe of inflammable air, that is to ſay hydrogene. I muſt firſt obſerve, that this ſuppoſition is by no means proved; and I will ſay even more, that it is not at all probable: but, even if it ſhould be eſtabliſhed and demonſtrated that hydrogene is a principle common to all combuſtible ſubſtances, to all thoſe bodies which have the property of decompoſing vital air or oxigenous gas, this will not at all invalidate the proof that the air is the true combuſtible, that this ſubſtance furniſhes the caloric and light during the act of combuſtion; and the antiphlogiſtic doctrine will not be leſs obliged to come to the aſſiſtance of the ancient doctrine to explain the phænomena of calcination and combuſtion. But I ſhall abſtain from the purſuit of theſe reflections in this place, and ſhall refer the reader to the proofs which the diſcuſſion will naturally bring forward in the courſe of this work.

SECTION

SECTION I.

OF THE

Weight of Different Sorts of Air.

AS I ſhall have frequent occaſion to calculate the weight of different kinds of air, in the ſequel of this treatiſe, it is proper to premiſe the means I uſed to aſcertain this weight.

Of Common Air.

Sir George Shuckburgh, by a ſeries of experiments made with a well-conſtructed barometer, diſcovered the length of a column of air, equiponderant with $\frac{1}{10}$ of an inch of mercury, whoſe ſpecific gravity was 13,6, at different barometrical heights, and in different temperatures; the weight of $\frac{1}{10}$ of an inch of mercury of that ſpecific gravity (which may be looked upon as conſtant, its variation being exceeding ſmall in the uſual temperatures of the atmoſphere) is 344,32 gr. Purſuing this

calculation, it will be found that 100 cubic inches of common air weigh *

Bar.	Therm.		Gr.
30	60°	- -	30,929
	50	- -	31,612
29,5	60	- -	30,414
	50	- -	31,124
Mean weight		- -	31,0197

As the barometer, both here and at Paris, generally ſtands at or between 29,5 and 30, and the temperature in our apartments is generally between 50 and 60°, I ſhall conſider the mean uſual weight of atmoſpheric air as 31 grains for every 100 cubic inches.

100 cubic inches of water weigh 25318 grains, and as 100 cubic inches of common air weigh 31 grains, it follows that common air is about 816 times lighter in the circumſtances above-mentioned than water. I have frequently weighed air in a glaſs globe containing about 116 cubic inches, and in general found the reſults to differ but little from thoſe reſulting from Sir George Shuckburgh's calculation, only always ſomewhat lighter, which I believe denotes an error rather in this method than in the barometrical: when Sauſſure's hy-

* See the reduction of the weights and meaſures to thoſe of France, at the end of this Section.—F. T.

gromete-

grometer was above 90° the air was *cæteris paribus* lighteſt.

Dephlogiſticated air.

I procured this air from præcipitate *per ſe*; its goodneſs was ſuch, that one meaſure of it and two of nitrous air left but $\frac{3}{10}$ of a meaſure: when 116 cubic inches of common air weighed 35,38 grains, 116 of this dephlogiſticated air weighed 39,03 grains, conſequently its weight is to that of common air as 1103 to 1000 nearly.

To find the quantity of moiſture in this air when produced over water, I filled a large jar, containing 81 cubic inches, with this air, and then raiſing it out of the water, I laid it on mercury over a ſaucer of three inches diameter, containing 256,8 grains of oil of vitriol, whoſe ſpecific gravity was 1,863, and left them together 24 hours; on withdrawing the ſaucer I found it to have gained 3,47 grains, conſequently 100 cubic inches may contain 4,32 of water. The temperature of the room was 58*.

To

* This quantity of water is much more conſiderable than M. de Sauſſeure found to exiſt in the air of the atmoſphere. The difference is even ſo great, that it is difficult to avoid ſuppoſing that ſome error has crept into the experiments. Beſides, it muſt not be thought that any ſubſtance can deprive the air of all its moiſture. It has already been obſerved, that the elective attractions act only by virtue of the exceſs of

one

To try whether the bulk of this air would be greater when obtained over water than when obtained over mercury, I diſtilled at the ſame time 240 grains of red precipitate over water, and in another retort of the ſame ſize, 240 grains over mercury, and found the quantity of air exactly the ſame. I could not fill ſo large a jar as one of the capacity of 81 cubic inches with mercury; but from this experiment, I am induced to think that dephlogiſticated air does not in a ſhort time abſorb more moiſture when received over water than when received over mercury.

Inflammable air.

The inflammable air uſed in this experiment was extracted from clean, newly made filings of ſoft iron, in the temperature of 59°, by vitriolic acid, whoſe ſpecific gravity was 1,0973, and obtained over mercury; it had ſcarce any ſmell, and that which it gave was very different from the uſual ſmell of inflammable air.

The barometer being 29,9, and the thermometer 60°, I found the weight of this air to

one affinity over another. The ſulphuric acid does not therefore take the whole of the water from air; but it is divided between the air and the acid until the two forces are in equilibrio. It may be obſerved, that air in general is ſpecifically lighter, when ſaturated with water, than when deprived of it. Note of the French tranſlator.

be

be to that of common air as 84,3 to 1000, conſequently nearly 12 times lighter.

I found that the bulk of inflammable air obtained from the ſame ſort and quantity of materials, with the aſſiſtance of heat towards the end, was nearly $\frac{1}{8}$ greater when it was obtained over water than when obtained over mercury. I have not weighed inflammable air thus obtained over water, but it is well known to be at moſt but 8 or 9 times lighter than common air.

From 85 cubic inches of inflammable air received over water, I extracted by oil of vitriol, in the manner above mentioned, in 55 hours, 2 grains of water; and though undoubtedly there is an error in all theſe experiments, yet there can be little doubt but this inflammable air contained $\frac{1}{2}$ its weight of water; the inflammable air by the ſubtraction of its water loſt its ſmell, but continued as inflammable as ever, and therefore there is no reaſon to think it was decompoſed, or that water is any way eſſential to it.

Phlogiſticated air.

By expoſing common air to a mixture of filings of iron and ſulphur made into a paſte, over mercury, I obtained air ſo far phlogiſticated that it was not in the leaſt diminiſhed by nitrous air; I dried it by frequently introducing

ducing dry filtering paper under the jar that contained it, and found its weight to be to that of common air as 985 to 1000, the barometer ſtanding at 30,46, and the thermometer at 60°: care muſt be taken that this air do not ſtand too long over the martial paſte, elſe inflammable air will be produced.

Alkaline air.

I found the weight of alkaline air to that of common air, to be as 600 to 1000, barometer 30, thermometer 61°: its weight probably varies in proportion to the moiſture it contains, which muſt be very conſiderable.

Nitrous air.

As nitrous air would infallibly diſorder the metallic apparatus of my globe for weighing airs, I endeavoured to find its weight by comparing the loſs of weight of the materials which produced it, viz. 50 gr. of copper, and 580 of nitrous acid, whoſe ſpecific gravity was 1,1389, with the volume of air produced. With this view I produced over mercury in the temperature of 64, barometer 29,6 in 8½ hours, 38,74 cubic inches of nitrous air, at the expence of 14 gr. of the materials; therefore 100 cubic inches of this air would weigh 36,1 gr. but 100 cubic inches of common

mon air would weigh but 30,2 gr. therefore the weight of nitrous is to that of common air as 1195 to 1000.

If this air had been obtained over water, or in ſtrong heat, its weight would probably have been very different, as it is liable to be mixed with phlogiſticated air, nitrous vapour, and a variable quantity of water: nitrous vapour would render it heavier, and phlogiſticated air or water probably lighter.

Fixed Air.

The barometer being at 29,85, and the thermometer 64°, I found the weight of fixed air extracted from calcareous ſpar, by marine acid, whoſe ſpecific gravity was 1,0145, and obtained over mercury, to be to that of common air as 1500 to 1000.

Notwithſtanding that this air was obtained in the drieſt manner poſſible, and that the globe which contained it appeared perfectly dry, yet when I carried it into a room 27 degrees colder, the inſide of the globe was covered with dew, which ſoon formed viſible drops.

Vitriolic Acid Air.

I extracted this air in a ſtrong heat from opper, by means of vitriolic acid, whoſe ſpecific gravity was 1,704. Its weight was to that of

of common air as 2265 to 1000, barometer 30,13, thermometer 60°.

The weight of this air muſt be ſomewhat variable, as it contains a variable proportion of water, and alſo of ſulphur.

Hepatic Air.

That extracted from ſulphurated iron, is to common air as 1106 to 1000; but as it contained a little metallic inflammable air, it is probably lighter than that drawn from alkaline or calcareous hepars.

Table of the abſolute weight of 100 cubic inches of different kinds of air, and their proportions to common air.

100 Cubic Inches.	Gr.	Proportion to common air.
Common air	31	1000
Dephlogiſticated	34	1103
Phlogiſticated	30,535	985
Nitrous -	37	1194
Vitriolic -	70,215	2265
Fixed -	46,5	1500
Hepatic -	34,286	1106
Alkaline -	18,16	600
Inflammable	2,613	84,3

By means of the 3d column, the weight of common air being rigorouſly given, that of any arti-

artificial air in the ſame temperature, and under the ſame preſſure, may be had pretty nearly; for it muſt be owned their expanſibility in different temperatures has not been as yet accurately determined: in point of compreſſibility, the difference is inconſiderable. I have ſet down the weight of dephlogiſticated and nitrous air ſomewhat lower than I found them, for the ſake of abridging calculation, and becauſe others have found their weight ſtill lower.

The mean weight of common air by Mr. Lavoiſier's calculation, differs very little from that which I aſſign to it, that is to ſay, only by 7 Troy grains, in a 1000 Engliſh cubic inches, his calculation exceeding mine by ſo much; but with reſpect to other airs, the difference between us is greater, as may be ſeen by the following table.

100 French cubic inches by my calculation.	French Gr.		By Mr. Lavoiſier.
Common air	45,69	-	46,81
Dephlogiſticated	50	-	47,317
Fixed air	68,74	-	69,50
Nitrous	54,53	-	40,

The weight of each of theſe airs being ſo different from that on which I grounded my former calculation of the proportion of their ingredients, I have been obliged to re-calculate the whole. To inflammable air, I ſtill aſſign the

the ſame weight as before, as it has not the great levity I found it to have, except it be made with particular care, ſo that I conſider it in the uſual ſtate as only ten times lighter than common air; I alſo conſider theſe airs as united with their uſual proportion of water, and not as perfectly pure. In ſuch circumſtances

100 cubic inches of	Gr.		Gr.	
Nitrous air contain	6,7	of phlogiſton and	30	of nitrous baſis
Fixed air -	8,14		38,36	dephlog. air

100 Gr. of				
Nitrous air -	18	-	82	nitrous baſis
Fixed air -	17	-	83	dephlog. air.

REDUCTION

REDUCTION

OF THE

Meaſures, Weights and Scales of Barometers and Thermometers, employed by Mr. Kirwan, to the Meaſures, Weights and Scales, commonly uſed in France, by Mr. Haſſenfratz.

I Have reduced all the meaſures of Mr. Kirwan to the royal foot, and for this purpoſe I have made uſe of the ſuppoſition, that the Engliſh foot uſed by Mr. Kirwan is in proportion to the French foot as 11,2596:12. This proportion was given me by Mr. de Lalande, from experiments made by himſelf on the compariſon of the meaſures of the two countries; whence it follows,

	French Inches.
That the Engliſh foot -	11,2596
the Inch - -	0,9383
the Line - -	0,0938
the Foot Square -	126,7795
the Inch Square -	0,8884
the Line Square -	0,0088
the Foot Cube -	1427,4864
the Inch Cube -	0,8260
the Line Cube -	0,0008

I have reduced the weights to the poids de marc, and have in the reduction made the ſuppoſition, that Mr. Kirwan always uſed Troy weight, and that the pound Troy, is equal to 12 oz. 1 gros, 47 grains poids de marc. I have taken this proportion from Mr. Tillet's Memoir, printed in the Memoirs of the Royal Academy of Sciences for the year 1767. Hence it follows,

	Grains.
That the pound of Mr. Kirwan	7031
the Ounce -	585,216
the Penny Weight or Denier	29,2958
the Grain -	1,22*

As Mr. Kirwan has conſtantly made his thermometrical obſervations after the ſcale of Farenheit, I have reduced thoſe obſervations to the temperature which would have been indicated by the gradation of Reaumur, by making uſe of the formul, $\frac{n-32\times 4}{9}$, ſuppoſing n to be the degree indicated by Farenheit's ſcale.

I have placed all the reductions, of the weights of the firſt ſection together, in the

* In Mr. Tillet's Memoir, the pound troy is one mark, 4 oz. 1 ½ gros, and 1 grain, which is 10 grains leſs than in the quotation of Mr. Haſſenfratz. Hence the pound will be equal to 7021 French grains, the ounce 585,083, the denier 29,254, the grain 1,215. This ſmall inaccuracy affects the whole of Mr. Haſſenfratz's reductions of weight.—Note of the Engliſh Tranſlator.

following

following note, becauſe theſe reductions appear to form a collection, which may be ſeparated from the ſection. I have been careful to refer to each article by letters*, for the more eaſy verification of the calculus: in future, the reductions will be placed at the foot of each page.

* As I perceive that the literal references have not been inſerted in the text, I have put numbers between the brackets to refer to the pages.—E. T.

(24) One hundred French cubic inches of common air weigh poids de marc—

Barometer. Inches	Thermometer.		
28,149	12,44 deg.	45,68	grains poid de marc.
	8,	46,69	
27,679	12,44	44,92	
	8,	45,97	
	Mean weight	45,81	

(24) 29.5 inches, and 30 inches of the Engliſh barometer, correſpond with 27.676 inches and 28.149 inches of the French barometer; and the 50 and 60 degrees of the thermometer of Fahrenheit anſwer to 8 and 12.44 degrees of Reaumur.

(24) One hundred cubic inches of water weigh 37419.8 grains poids des marc, and one hundred cubic inches of common air weigh 45.81 grains; the proportion therefore is 816:6.

(25) When 95.816 cubic inches of common air weigh 43.36; 95.816 cubic inches of dephlogiſticated air weigh 47.61: the proportions therefore are nearly 1104:1000.

(25) One hundred French cubic inches may therefore, according to Mr. Kirwan, contain 6,38 grains of water, the temperature being 9.777.

(26) Two hundred and ninety-two grains of the red oxide of mercury afforded therefore 66.906 cubic inches of dephlogiſticated air.

(26) The temperature at which the inflammable gas was produced was 12 degrees of Reaumur, and at the time of weighing it the temperature was 12.44, and the barometer ſtood at 28.149.

(27) Seven thouſand and twenty-ſeven * cubic inches of inflammable gas loſt 2.95 grains of water by expoſure to the vitriolic acid.

(28) When the weight of the phlogiſticated air was taken, the barometer ſtood at 28.58 inches, and the thermometer at 12.44 degrees.

(28) The weight of alkaline gas was taken at the preſſure of 28.149 inches, and temperature of 12.88.

(28) Fifty-one grains of copper in 707.6 grains of nitrous acid, whoſe ſpecific gravity was 1.1389 produced 31.999 cubic inches of nitrous gas, the barometer ſtanding at 27.773 in and the thermometer at 14.222. The loſs of weight during the operation was 17.08 grains, whence the weight of 100 cubic inches proves to be 53.3 grains. The weight of 100 cubic inches of common air being 44.6, it follows that the ratio of the former to the latter is 1195 : 1000.

(29) The ſpecific gravity of fixed air was taken at a preſſure of 28 inches, and temperature 14.222.

(30) The barometer ſtanding at 28.27, and the thermometer 12.44, the weight of the vitriolic acid air was to that of common air as 22.65 to 1000.

(30) A table of the abſolute weights of 100 cubic inches of the different kinds of air in French weights and meaſures, according to Mr. Kirwan.

Common air	45.81	1000
Dephlogiſticated	50.52	1103
Phlogiſticated	45.192	985
Nitrous	54.69	1194
Vitriolic	103.759	2265
Fixed	68.715	1500
Hepatic	50.665	1106
Alkaline	27.486	600
Inflammable	3.861	84.3

As all the experiments hitherto made upon the compoſition of common air, appear to eſtabliſh that 100 cubic inches conſiſt of 28 inches dephlogiſticated and 72 of phlogiſticated air, it would follow on the ſuppoſition that the two airs were accurately weighed, and that no combination took place between them, that 100 cubic inches of common air would weigh 46.68 grains, and if any ſmall degree of combina-

* An overſight; it ſhould be 70.21 cubic inches.—T.

tion

tion ſhould take place, the weight would be proportionably increaſed.

(31) According to the experiment of Mr. Lavoiſier, (ſee the Memoirs of the Royal Society of Medicine for the year 1782, page 569) one hundred cubic inches of common air, at the temperature of 10 degrees of Reaumur's thermometer, and at the preſſure of 28 inches, weigh 46 grains.

One hundred cubic inches of vital air, or oxigenous gas, at the ſame temperature and preſſure, weigh 50 grains.

One hundred cubic inches of mephitis, phlogiſticated air, or azotic gas, weigh 44 grains.

Since the impreſſion of theſe reſults, Mr. Lavoiſier has endeavoured to determine the ſpecific gravity of vital air or oxigenous gas with more preciſion than before, by keeping an account of the ſmall quantity of mephitis, or azotic gas, which it almoſt always contains; and he thinks that the weight of 100 cubic inches of this air may be ſet at 51 grains. A greater weight indicates a mixture of carbonic acid gas; a leſs weight indicates a mixture of azotic gas.

The airs in theſe reſults are ſuppoſed to be ſaturated with water. Their volume is changed nearly $\frac{1}{215}$ for each degree of Reaumur when the temperature is altered.

(32) One hundred cubic inches of nitrous air contain 9.9 grains of phlogiſton, and 44.79 of nitrous baſis.

One hundred cubic inches of fixed air contain 12.0288 grains of phlogiſton, and 56.687 of dephlogiſticated air, according to the opinion of Mr. Kirwan.

SECT. II.

Of the Compoſition of Acids, and General Principles of the New Theory.

WITH reſpect to the nature and internal compoſition of acids, it muſt be owned that the theory of chymiſtry has been much advanced by the deductions and reaſonings of Mr. Lavoiſier: that a certain quantity of pure air diſappeared during the combuſtion of ſulphur and phoſphorus, and on uniting pure air with nitrous air, was firſt diſcovered by Dr. Prieſtley; but the connection and relation of this air to the reſulting acids, was firſt attended to by Mr. Lavoiſier. I have ſhewn in different papers, in the Philoſophical Tranſactions, that this air always unites to the phlogiſtic principle, and is converted into fixed air, but I neglected tracing it any farther; I am now of opinion that it becomes an eſſential conſtituent part of acids.

All acids conſiſt of two principles, one peculiar to each, which, in the opinion of the antiphlogiſtians, has not as yet been decompoſed, and conſequently muſt be looked upon, relatively to the preſent ſtate of our knowledge, as a *ſimple* ſubſtance; and the other, *pure air* in a concrete ſtate, that is, deprived of the greater

greater part of its ſpecific heat, and condenſed into a ſmaller volume; the firſt they call the acid *baſis*, the laſt, the *oxigenous* principle; thus the vitriolic acid, according to them, conſiſts of *ſulphur* as its baſis, and pure air, in a concrete ſtate, as its *acidifying* or *oxigenous* principle.

This doctrine of the compoſition of acids has been admitted by ſome of the ableſt defenders of phlogiſton, and particularly by that diſtinguiſhed philoſophic chymiſt Mr. de Morveau, with this ſingle modification, that the baſes of acids contain phlogiſton, which they loſe on uniting to pure air; yet it ſeems to me very difficult to conceive how pure air can unite to phlogiſton, a ſubſtance to which it has the greateſt affinity, without forming a new compound, endowed with very different properties from thoſe which it poſſeſſed before ſuch union; it ſeems, therefore, more reaſonable to conclude, either that it forms water, as Mr. Cavendiſh thinks, or fixed air, as I ſhall endeavour to prove in the following ſections. It muſt be allowed, that the conſtant extraction of fixed air from the vegetable acids, and the impoſſibility of procuring pure air from them, forms a ſtrong preſumption in favour of this laſt opinion.

Table of the affinities of the oxigenous principle, according to Mr. Lavoiſier, Mem. Par. 1782, p. 535.

Baſes.	Reſulting Compounds.
Baſis of the marine acid	Dephlog. marine acid
Charcoal - -	Fixed air
Zinc - - -	Calx of zinc
Iron - - -	Calx of iron
Inflammable principle	Water
Regulus of manganeſe	Calx of manganeſe
Cobalt - - -	Calx of cobalt
Nickel - -	Calx of nickel
Lead - - -	Calx of lead
Tin - - -	Calx of tin
Phoſphorus - -	Phoſphoric acid
Copper - -	Calx of copper
Biſmuth - -	Calx of biſmuth
Regulus of antimony	Calx of antimony
Mercury - -	Calx of mercury
Silver - - -	Calx of ſilver
Regulus of arſenic	Calx of arſenic
Sugar - - -	Acid of ſugar
Sulphur - -	Acid of vitriol
Nitrous air - -	Acid of nitre
Principle of heat -	Dephlogiſticated air
Gold - - -	Calx of gold
Smoking marine acid	
Nitrous acid	
Black calx of manganeſe	

This

This table is liable to numerous objections, which I ſhall have occaſion to mention in the ſequel; I ſhall here mention only a few which apply generally to the whole table.

1ſt. Of the firſt 19 ſubſtances which have the greateſt affinity to the oxygenous principle, not one unites to it in the common temperature of the atmoſphere; and yet nothing prevents this union but the affinity of the principle of heat with the oxygenous principle, which affinity is laid down in this table as weaker than that of any of the nineteen ſubſtances that precede it.

2dly. The only ſubſtance which unites to the oxygenous principle in every temperature, and conſtantly expels the principle of heat, is nitrous air *, which yet, in this table, is ſet down as having almoſt the weakeſt affinity with the oxygenous principle.

3dly. No proof is given that pure air, while pure air and uncombined with any other ſubſtance, unites to any thing except inflammable air; nor has it been produced from any ſubſtance except the calces of the perfect metals, mercury and lead, unleſs they were previouſly combined with ſome acid.

* Nitrous air expels only a very ſmall portion of heat in vital air or oxygenous gas. This ſame heat appears again in all the decompoſitions of the nitrous acid, and is even capable of being meaſured.—Note of the French Tranſlator.

Of

Of the Compoſition and Decompoſition of Water.

The experiments of Mr. Cavendiſh, and of Mr. Monge, appear to me to leave no room to doubt that when very pure dephlogiſticated air and inflammable are inflamed, the product is mere water; for when theſe airs are employed in the proper proportion, only $\frac{1}{100}$ of the mixture of both airs retains its aerial form*; now it is impoſſible to ſuppoſe that all the water obtained pre-exiſted in theſe airs, that is, that 49 parts in 50 were water.

According to Mr. Lavoiſier, 100 parts of water by weight, contain about 87 of dephlogiſticated air, and 13 of inflammable air, that is, nearly in the proportion of 7 to 1†; and ſuppoſing the weight of theſe airs to be ſuch as given in the firſt ſection, 100 troy gr. of water will contain 254,4 cubic inches of dephlogiſticated air, and 497 of inflammable air‡, that is nearly as 1 to 2; however,

* Philoſophical Tranſ. 1784, p. 134.

† The experiments made at the beginning of the year 1785, in the preſence of the Commiſſion of the Academy of Sciences at Paris, give about 85 parts by weight of vital air, and 15 of inflammable gas. This experiment may be conſidered as equally exact with that of Mr. Monge.—Note of the French Tranſlator.

‡ Whence 100 gr. poids de marc contain 2101.34 of oxygenous gas, and 417.522 of hydrogenous gas.

this

this calculation is ſomewhat precarious, as it is grounded chiefly on the experiment of Mr. Monge, the moſt accurate of thoſe made in France; and his inflammable air was certainly ſaturated with water, its ſpecific gravity being not quite ſeven times below that of common air*.

The only circumſtance in which water has clearly been proved to reſult from the union of inflammable and dephlogiſticated air, is that in which one or both were expoſed to a red heat, but it cannot fairly be inferred that water reſults from their union in any lower heat; on the contrary, it appears that another compound of both, viz. fixed air, is then formed; thus mercury and ſulphur in a low heat form æthiops, and in a greater cinnabar; yet it is certain that in low heats, both theſe airs may remain long together without forming any union, and when they do unite, it is becauſe one of them has not its whole quantity of ſpecific fire; but in high degrees of heat, their *ſpecific* becomes *ſenſible* heat, as Mr. Watt has diſcovered†. How great an impediment ſpecific heat is to the union of bodies, when the compound that ſhould reſult from ſuch union muſt contain much leſs of it than either of the ingredients, I have elſewhere ſhewn by the ex-

* Mem. Par. 1783, p. 79.
† Philoſophical Tranſ. 1784, p. 335.

ample

ample of fixed air and quicklime, and oil of vitriol and water *.

Another principle aſſumed by the patrons of the new theory, and which indeed is the corner ſtone of their whole ſyſtem, is the *decompoſition* of water, but of which the maintainers of the old doctrine have as yet received no ſatisfactory proof; according to Mr. Lavoiſier's table, water ſhould be decompoſed by charcoal at leaſt in a boiling heat, which is full ſufficient to communicate as much ſpecific heat to the inflammable part of water as is neceſſary to its aerial form: yet water has not yet been decompoſed in that manner; whereas water and iron will produce inflammable air in the temperature of the atmoſphere, though iron has in his ſyſtem leſs affinity to the oxigenous principle than charcoal has to that principle, an evident ſign that it is not from the water, but from the iron, that the inflammable air proceeds.

* Philoſophical Tranſ. 1784, p. 168.

NOTE

NOTE

OF

MR. LAVOISIER.

MR. Kirwan, in the defects which he urges againſt the table of affinities of the oxigenous principle with the different ſubſtances, does not judge me with more ſeverity than I do myſelf. But he ought to have taken notice that I had myſelf made all the objections he urges againſt this table before him, and perhaps in a ſtronger manner. The following is the manner in which I expreſſed myſelf in the Memoirs of the Academy of Sciences for the year 1782, beginning at page 530.

" I am not unacquainted with the difficul-
" ties which attend the conſtruction of a table
" of affinities; and, in order that it may not be
" thought that I am diſpoſed to conceal them,
" I ſhall proceed to exhibit them in all their
" force. A principal defect, common to all
" the tables of affinities which have hitherto

" been

" been made, conſiſts in their preſenting only " the reſults of ſimple affinities, whereas there " exiſts only in nature, as far as we can ob- " ſerve them, caſes of double affinity, often " triple, and others perhaps ſtill more com- " plicated.

" To form accurate ideas reſpecting theſe " phenomena, it is neceſſary to conſider all " the bodies in nature as plunged in an elaſtic " fluid of great rarity and lightneſs, known by " the name of the igneous fluid, or principle " of heat. This fluid, which penetrates all " bodies, tends continually to ſeparate their " parts, and would ſeparate them if they were " not retained by their mutual attraction, that " is to ſay, the attraction which is commonly " called the affinity of aggregation. The re- " ſiſtance which the conſtituent molecules of " bodies oppoſe to their ſeparation, is therefore " the reſult of two forces, both of which are " variable; the firſt, according to a certain " law dependant on the temperature; and the " ſecond, according to the diſtance to which " the action of the igneous fluid may remove " the particles from each other. It is in " conſequence of theſe two cauſes, that the " ſame body, more or leſs heated, becomes " ſucceſſively ſolid, liquid, or aeriform, accord- " ingly as the effort which the matter of fire " makes to ſeparate the parts is more or leſs " ſtrong, or weak, or in equilibrio with the " aggregative force. I have ſpoken elſewhere " of another cauſe which oppoſes the ſepara-

" tion

" tion of the molecules of bodies, and prin-
" cipally of fluids, viz. the preſſure of the at-
" moſphere.

" Hence it is diſtinguiſhed, that when two
" bodies are combined together, their action
" is abſolutely different according to the de-
" gree of heat in which the combination is
" made. If they be both concrete, as for ex-
" ample, lead and tin, they have no action
" upon each other, becauſe the attraction of
" their reſpective parts amongſt themſelves is
" ſtronger than the mutual action which the
" molecules of the two metals can exerciſe
" upon each other; ſo that it becomes a
" chymical axiom *corpora non agunt niſi ſint*
" *ſoluta:* but when by a ſtronger action of
" heat the molecules of one of the two me-
" tals have been ſeparated; where their at-
" traction or affinity of aggregation has been
" diminiſhed, then they act on each other,
" and combination takes place between the
" two metals.

" A table of affinities cannot therefore pre-
" ſent true reſults but at a certain degree of
" heat. Mercury affords a ſtriking inſtance
" of this. Let this metal be heated to ſuch
" a degree as to make it boil; it will then de-
" compoſe vital air, and ſeize the oxigenous
" principle, which is one of its conſtituent
" parts, and will by that means be calcined,
" and become converted into the red calx of
" mercury. If a ſomewhat ſtronger degree
" of heat be uſed; namely ſuch as is ca-

" pable of ſoftening glaſs, the vital air is diſ-
" engaged, and the mercury is revived. We
" ſee therefore, that at the temperature of
" boiling mercury, the oxigenous principle
" has a ſtronger affinity with the metal than
" the matter of heat has, and that the contrary
" takes place at a more elevated tempera-
" ture.

" A table of affinities conſtructed upon the
" principles of all the facts we are acquaint-
" ed with, cannot, however, expreſs more
" than one of theſe two effects, and muſt
" therefore be neceſſarily defective in one or the
" other caſe. Mr. Bergman has endeavoured
" to remedy this inconvenience, by dividing
" his table of affinities into two parts, the one
" intended to exhibit the reſults of experi-
" ments in the humid way, and the other in
" the dry way. But to obtain tables which
" ſhall ſtrictly agree with experiment, it is
" neceſſary, as it were, to form a table for
" each degree of the thermometer.

" A ſecond defect of our tables of affinities
" is, that they take no account of the effects
" of the attraction of water, and perhaps its de-
" compoſition, in its combinations by the hu-
" mid way. Water is conſidered as an agent
" ſimply paſſive, though it acts with a real
" and diſturbing force, which ought to be
" brought into conſideration in the reſults.

" A third imperfection of tables of affini-
" ties is, that they cannot expreſs the varia-
" tions

" tions which take place in the attractive " force of the molecules of bodies, at the dif- " ferent degrees of ſaturation. There are " certain combinations which have two or " three evident degrees or periods of ſatura- " tion, and there are others in which a greater " number obtain: the formation of acids af- " fords many examples upon which it may " not be uſeleſs to digreſs for a moment. The " vitriolic acid, as I have ſhewn in a Memoir " in the collection for the year 1777, is pro- " duced by the union of ſulphur and oxigene; " but by the combination of theſe two prin- " ciples, it is poſſible to form two diſtinct " acids, which differ eſſentially from each " other in moſt of their properties; the vi- " triolic acid, which is ponderous, fixed, with- " out ſmell, and attracts water with great " avidity; the ſulphureous acid, which is " eminently volatile, does not combine with " water, but in a ſmall quantity, and has a " very penetrating ſmell: theſe two acids " have each their degree of ſaturation; the " firſt conſtitutes the ſulphureous acid, and " the latter the vitriolic acid, without there " being any intermediate compound between " the ſulphur and the ſulphureous acid, or " between this laſt and the vitriolic acid; and " in order to convert the one into the other, " it is ſufficient if oxigene be added to the " ſulphureous acid, or taken from the vitriolic " acid.

" The marine acid, as I have already " obſerved, preſents the ſame phenomenon; it " is compoſed of an unknown principle, which " has not yet been obtained in a diſengaged " ſtate, but in the acid is combined with ox " igene: if this acid be applied to manganeſe, " or other metallic calces, as it has a greater " affinity than moſt of them with oxigene, it " ſeizes this principle, and becomes com- " pletely ſaturated; it then forms a gaſeous " acid, capable of being abſorbed to ſaturation " by water, and poſſeſſing the property of " diſſolving gold, &c. It is this acid which " Meſſrs. Bergman and Scheele have named " the dephlogiſticated marine acid. On the " contrary, in the ſtate wherein the acid is " obtained by diſtillation from ſea ſalt, whe- " ther with clay or the vitriolic acid, it is not " completely ſaturated with oxigene; it is " then analogous to the ſulphureous acid, is " very volatile, has a penetrating ſmell, &c. " It is very probable that the ſame circum- " ſtances take place in the two phoſphoric " acids, namely, that obtained by perdeli- " quium, and that obtained by combuſtion; " the firſt is much leſs ſaturated with oxigene " than the ſecond, and there exiſts the ſame " difference between them, as between the " ſulphureous and vitriolic acids.

" Laſtly, nitrous air is capable of taking " with oxigene, not only two, but an infinity " of degrees of ſaturation: and there reſults

" an

" an infinity of different nitrous acids, from " that which is called dephlogiſticated, and " is white and colourleſs, to that which is the " moſt red and ſmoking.

" It may eaſily be conceived, that the force " of affinity, which unites the two principles, " ſulphur for example with oxigene, is not " the ſame in the two degrees of ſaturation, " in the vitriolic acid and the ſulphureous " acid; but this difference is the more parti- " cularly remarkable in the nitrous acid. Ni- " trous air, which adheres ſtrongly to this " acid when it is completely ſaturated with " oxigene, is retained with very little force in " the fuming nitrous acid, ſince the ſimple " heat of the atmoſphere is ſufficient to ſe- " parate it. I might add, that this difference " in the proportion of oxigene, changes the " affinities between the acid and the diffe- " rent ſubſtances with which it is capable of " uniting; that the acid, which was the ſtrong- " eſt when completely ſaturated with this " principle, becomes weaker in proportion as " it is deprived of it; but I ſhould depart " from the object of this Memoir, which is " only to examine the degrees of affinity of " oxigene with different ſubſtances, and not " the degrees of affinity which thoſe ſub- " ſtances acquire by being combined with that " principle.

" What I have here ſaid againſt tables of " affinities, naturally applies to that which I

" preſent; but I am nevertheleſs of opi-
" nion, that it may be of ſome uſe, at leaſt un-
" til a greater number of experiments, and
" the application of mathematics to che-
" miſtry, ſhall enable us to extend our views.
" At ſome future time, the preciſion of our
" data may perhaps be carried to that degree,
" that the geometer may calculate in his clo-
" ſet the phenomena of particular chemical
" combinations, in the ſame manner as he now
" computes the motions of the celeſtial bo-
" dies. The views which Mr. de la Place
" entertains reſpecting this object, and the
" experiments we have projected according to
" his ideas, to expreſs by numbers the forces
" of affinity between different bodies, give us
" reaſon already to conſider this as a hope not
" entirely chimerical."

I did not preſume to offer a table of the affi-
nities of oxigene with different ſubſtances, till
after I had made theſe preliminary obſerva-
tions; and certainly it could not have been
done with more reſerve and circumſpection.
At this day, when I review theſe reflections,
more than four years ſince they were drawn
up, and after having been inſtructed by the
criticiſm of Mr. Kirwan, I ſcarcely ſee any
thing to add to them. I ſhall inſiſt only upon
two points, which I at that time mentioned
only in a ſummary way, but which require to
be developed ſomewhat more amply.

It would be a falſe idea of the affinities, if

any

any one ſhould perſuade himſelf, that in all caſes a body will take from another the whole of a principle for which it has a greater affinity. Let us clear up this enunciation by examples. If the ſulphuric acid be boiled upon mercury, ſilver, or copper, theſe metals do not completely decompoſe the acid; they do not take from the ſulphur the whole of the oxigene to which it was united; for they act upon the oxigene only by virtue of the attractive force they exerciſe upon it diminiſhed by the attractive force which the ſulphur exerts upon the ſame principle. The oxigene, in theſe kinds of decompoſitions, muſt be conſidered as obedient to two unequal forces; on the one part, it is attracted by the metal which tends to calcination, that is to ſay, to become an oxide; and on the other, it is retained by the ſulphur: and it is divided into two parts, until an equilibrium is obtained. When therefore the table of affinities announces that ſilver, mercury, and copper, deprive ſulphur of the oxigene, the event is not accurately expreſſed; for it ought to be ſaid, that when theſe metals are preſented to oxigene and ſulphur, the oxigene is divided between the ſulphur and the metals in a certain proportion, which conſtitutes an oxide and ſulphureous acid. Now if we could ſuppoſe that the form hitherto given to our tables of affinities, could expreſs this mixed effect in the ſimple caſe I have related, yet there are an infinity of others

more complicated, to which the language of our tables is abſolutely inapplicable.

I muſt add, in the ſecond place, that at the time in which I drew out the Memoir upon the affinities of oxigene, the decompoſition of water was only a conjecture. This is now proved, and at preſent obliges us to conſider in a very different manner all the affinities which take place when metals are diſſolved in diluted acids. It is impoſſible to avoid the conſideration of the affinity which the principles of water have with reſpect to themſelves, or with the metals, or with the conſtituent principles of the acids; and the complication which reſults in the effects, gives riſe to an infinity of anomalies which are difficult to be accounted for, and ſtill more difficult to be foreknown in the actual ſtate of our knowledge, and which cannot poſſibly be expreſſed in our tables of affinities.

This is all I ſhall add at preſent to the general and preliminary reflections, which are placed at the head of the Memoir I publiſhed upon this ſubject, in the volume of 1782. They tend to confirm the truth, that it is impoſſible to make an exact table of affinities in the form hitherto adopted, and in the preſent ſtate of our knowledge. So that to reſume what has been ſaid, the table I have preſented affords true reſults only in certain degrees of temperature. It does not expreſs that one body takes from another the whole of the oxigene

igene which was combined with it; but only that this principle is divided between the two, until the point of equilibrium; and, laſtly, I could not attend in its conſtruction to an infinity of diſturbing cauſes, ſuch as the action of water, and the principles which compoſe it. But the cauſes of error and uncertainty are common to all the tables of affinities hitherto publiſhed, and may be more eminently urged againſt the column of affinities of phlogiſton, publiſhed by Mr. Bergman, of which mine is in many reſpects merely an inverſion.

After theſe general reflections, I think myſelf diſpenſed from diſcuſſing the objections of Mr. Kirwan, article by article. I have only to complain, that after having proved that certain articles of my table of affinities affords falſe reſults in ſome circumſtances, as I had myſelf before announced, he afterwards ſuppoſes them true, in order to argue in favour of phlogiſton; but it will be eaſy for me to diſconcert this manner of reaſoning, ſince it is a principle in ſound logic, that a juſt concluſion cannot be drawn from a fact which is conſidered as falſe, nor from a principle which the reaſoner conſiders as erroneous.

NOTE

OF

MR. LAVOISIER,

Upon the Decompoſition and Recompoſition of Water.

MR. Kirwan agrees with us in this article, that water is a compound of dephlogiſticated air and inflammable gas, or, according to our manner of expreſſion, of oxigene and hydrogene; we have therefore no reply to make on this head. But he thinks that, from this combination of oxigene and hydrogene, there does not always reſult water; that in ſome circumſtances the reſult is fixed air, or carbonic acid; that in others it is phlogiſticated air, or azotic gas; and, laſtly, that the reſult is ſometimes nitrous gas and nitrous acid. All theſe ſubſtances, according to Mr. Kirwan, are compoſed of the ſame principles; in the ſame manner, for example, as ſulphur and mercury afford either ethiops

ethiops or cinnabar, according to the degree of heat. It is upon this article that we differ eſſentially from the opinion of Mr. Kirwan. We maintain, that when pure inflammable air is employed, that is to ſay, exempt from all mixture of phlogiſticated air; or of charcoal, and is combined at any degree of heat whatever with perfectly pure vital air, or oxigenous gas, water is conſtantly formed, and the weight of this water is rigorouſly equal to the weights of the two airs. We will even go further: we will ſhew, in the diſcuſſion of the experiments of Mr. Kirwan, that univerſally whenever he obtained fixed air, or carbonic acid, charcoal was preſent; and that whenever charcoal was not preſent, the carbonic acid was not formed; laſtly, that it is a gratuitous and unfounded ſuppoſition, that inflammable gas or hydrogene is one of the elements of charcoal.

With regard to the decompoſition of water, which Mr. Kirwan denies, the laſt experiment which was made at Paris in the preſence of a numerous commiſſion of the Academy of Sciences, does not permit any longer doubt. The long abſence of M. Meuſnier, one of the co-operators in this experiment, has prevented its being yet publiſhed. The following is an abridged account.

A gun-barrel was taken, into which was introduced a quantity of thick iron wire, flattened by hammering; the gun-barrel, and the iron

iron which it contained, were weighed with the moſt ſcrupulous exactneſs; after which the outſide of the gun-barrel was covered with a lute, for the purpoſe of ſecuring it from the immediate contact of the fire. It was then placed in a furnace with ſuch a degree of inclination, that water could run through it. To the higher extremity was adapted a funnel intended to contain water, which was ſuffered to eſcape drop by drop by means of a cock. This funnel was cloſed to prevent all evaporation of the water. To the inferior extremity of the ſame gun-barrel was luted a tubelated receiver, deſigned to receive the water which ſhould eſcape decompoſition. Laſtly, to the tube of the receiver was fitted another tube to convey the hydrogenous gas to the pneumato-chemical apparatus.

As a further precaution, a vacuum was made in every part of the apparatus, in order that the hydrogenous gas might not be mixed with common air; laſtly, when all theſe preparations were completed, the gun-barrel was made red hot, and the water introduced drop by drop. An enormous quantity of inflammable gas or hydrogene was diſengaged during the courſe of the experiment. When it was finiſhed, the gun-barrel was cleared of its lute, and being weighed, was found to have acquired a very conſiderable augmentation of weight: this augmentation of weight, added to that of hydrogenous gas obtained, gave a total very exactly

exactly equal to that of the water which had diſappeared. With regard to the flat pieces of iron which had been introduced into the gun-barrel, and likewiſe the interior part of the barrel itſelf, they were found converted into a thick ſtratum of black oxide of iron or martial ethiops, cryſtallized like the iron ore of Elba. The chemical analyſis of this ſubſtance proved that the iron was reduced exactly to the ſame ſtate as that which had been burned in vital air or oxigenous gas; or, in other words, it conſiſted of iron combined with oxigene.

Demonſtrative as this experiment was, it was not ſufficient to content the chymiſts who made it: they were deſirous of forming water again with the ſame hydrogenous or inflammable gas which had been obtained; it was burned in an apparatus properly ſuited to this purpoſe, with a quantity of oxigenous gas equal to that which had been retained by the gun-barrel, and the ſame quantity of water was reformed with ſufficient exactneſs, and amounted to a little more than ſix ounces. This double experiment, one of the moſt memorable which was ever made, on account of the ſcrupulous exactneſs which was attended to, may be regarded as a demonſtration of the poſſibility of decompoſing and recompoſing water, and of its reſolution into two principles, oxigene and hydrogene, if in any caſe the word Demonſtration may be employed in natural philoſophy and chemiſtry.

To

To ſuch deciſive experiments Mr. Kirwan oppoſes an argument drawn from the order in which I have arranged the different ſubſtances in the table I publiſhed of the affinities of the oxigenous principle. Charcoal, according to this table, has a greater affinity with oxigene than iron: now iron, according to my experiments, decompoſes water in the common temperature of the atmoſphere; whence charcoal ought likewiſe to decompoſe water in the cold, or at leaſt in a boiling heat. To this I ſhall anſwer, as I have already done, that theſe anomalies of the affinities abſolutely depend on the degree of temperature. It cannot be doubted that the charcoal, at a red heat, takes oxigene from all metallic ſubſtances; this is a fact againſt which no exception can be made, and it is the foundation of the whole theory of metallic reduction: but this action of charcoal upon oxigene, this property which it poſſeſſes of taking it from metallic ſubſtances, is not ſo ſtrong in the cold as at a red heat, ſince we are unacquainted with any metallic revivification effected by charcoal without heat.

This, which is true with regard to metallic oxides, is equally ſo with reſpect to water; charcoal, which decompoſes it eaſily and inſtantly at a red heat, has only a ſlow and almoſt inſenſible action upon that fluid at the ordinary temperature of the atmoſphere. I ſay an action almoſt inſenſible, becauſe this

action

action is not abſolutely ſo. Mr. Gengembre has obſerved, that if charcoal be immerſed in water, and kept at a temperature of 30 degrees of the thermometer of Mr. de Reaumur, the water is gradually decompoſed, and inflammable gas is formed. Beſides, as I have already obſerved, the difficulties which may preſent themſelves in the explanation of ſome particular facts, cannot either deſtroy or ſhake truths which are ſolidly eſtabliſhed, and founded upon deciſive experiments. It is a principle, that an opinion cannot be refuted but by proofs of the ſame kind as thoſe which were uſed in eſtabliſhing it. The proofs which we have given of the decompoſition and recompoſition of water being of the demonſtrative order, it is by experiments of the ſame order, that is to ſay by demonſtrative experiments, which they ought to be attacked. All the objections hitherto oppoſed againſt them, are ſo far from poſſeſſing the ſlighteſt character of demonſtration, that they barely amount to ſlight probabilities.

SECT.

SECT III.

Of the Vitriolic Acid.

ACCORDING to the new theory, this acid conſidered abſtractedly from the water which it always contains, conſiſts of ſulphur (which is conſidered as a ſimple ſubſtance) united to a large proportion of the oxigenous principle. In my opinion, it conſiſts of a *baſis* or radical principle, which, when ſaturated with phlogiſton, conſtitutes *ſulphur*; when ſaturated with fixed air, becomes common *fixed vitriolic acid*; and when combined partly with the one and partly with the other, becomes *volatile vitriolic acid:* ſo that volatile vitriolic acid is nothing elſe but common vitriolic acid holding ſulphur in ſolution. This view of the volatile acid I owe to Mr. Berthollet, and it ſeems to be the only improvement made in its theory ſince the days of Stahl.

That ſulphur during its converſion into vitriolic acid, unites to air of ſome ſort or other, is evident from the quantity of air which it abſorbs in whatever way that converſion is brought about. Thus, firſt, during combuſtion in reſpirable air, I have ſhewn that 100 gr. of ſulphur

ſulphur abſorb 420 cubic inches of pure air, or about 143 gr.* but the proportion of this pure air actually united with a given quantity of ſulphur, is not eaſily determined, becauſe it is vitriolic air that is conſtantly formed, and this air eſſentially contains ſome portion of ſulphur in ſolution, which portion is variable. Secondly, Pyrites, during their decompoſition, abſorb a conſiderable proportion of pure air, as Mr. Lavoiſier has obſerved, ſo alſo does liver of ſulphur expoſed to the atmoſphere, for after ſome time it is converted into tartar vitriolate.

But whether the pure air thus abſorbed remains pure air, or is converted into fixed air or water, is not agreed upon: that it is converted into fixed air ſeems to me moſt probable from the following facts:

1ſt. I took 60 gr. of red precipitate, and 12 of flowers of ſulphur, and having well mixed them, I diſtilled them with a gentle heat from a glaſs retort, whoſe capacity with that of its adopter was 6,18 cubic inches, and received the air over mercury: 1½ cubic inch firſt paſſed, which was nothing elſe but part of the air of the veſſels; after this a ſlight inflammation took place in the retort, accompanied with a rapid production of air and white fumes, and part of the maſs ſublimed into the neck of the

* Which makes 346,92 French cubic inches, weighing 174,46 grains poids de marc.

retort.

retort. The quantity of air now obtained, added to that had before inflammation, amounted to 6½ cubic inches, then changing the receiver by a greater heat, and without any inflammation, 10 cubic inches of air paſſed clear and colourleſs. Of the 16½ cubic inches thus produced, I found 14 to be vitriolic air, being abſorbed by the ſolution of marine baroſelenite; one continued unabſorbed until lime water was added; the remainder was worſe than common air *.

From this experiment I infer, that the air that united to the ſulphur was fixed air, for if it had been pure air, the combuſtion muſt have continued during the whole time of their union. It is to no purpoſe to ſay that this combuſtion was prevented by the preſence of the vitriolic air, for if this air could prevent the combuſtion (that is, the expulſion of heat and light from the pure air), it ſhould alſo prevent the union of the pure air and ſulphur, juſt as it does when ſulphur is burned in pure air; but ſince an union took place without the expulſion of heat and light, it is evident that the air which entered into this union was not pure air, and by the ſame reaſoning it follows that water was not produced; the firſt inflammation aroſe

* That is in French meaſures 73,2 grains poids de marc of red oxide of mercury, and 14,64 of flowers of ſulphur in a retort, whoſe capacity was 5,1 cubic inches. M. Kirwan obtained 13,629 cubic inches of gas, of which 11,563 was ſulphureous acid gas.

from

from the common air of the veſſel. The diminution by lime water ſhews alſo that ſome uncombined fixed air remained. In this experiment the ſulphur was decompoſed, its phlogiſton uniting to the mercury, and its baſis to the fixed air contained in the mercurial calx: ſome part remained undecompoſed, and contributed to the formation of the vitriolic air.

2dly. I have already mentioned, in my Treatiſe on Hepatic Air, that 6 cubic inches of vitriolic air, and 5 of hepatic air, left a reſiduum of fixed air, which muſt have been contained in the vitriolic air.

3dly. Doctor Prieſtley conſtantly obtained a reſiduum of fixed air from the diſtillations of the vitriols of iron, copper, or Mercury. 3 Prieſtley, 216,227. Mr. Lavoiſier obſerved, that the dephlogiſticated air obtained from vitriol of mercury precipitates lime water. Mem. Par. 1777, p. 327. If ſulphur be burned in a large quantity of dephlogiſticated air, ſome fixed air is always found in the reſiduum. 6 Pr. 267.

4thly. If the vapour of oil of vitriol be made to paſs through a red hot earthen tube, a quantity of fixed air will be obtained. 1 Chy. Annals 1785, p. 523.

5thly. If ſulphur be digeſted in oil of turpentine, and then ſlowly diſtilled for 10 or 12 days, it will be converted into vitriolic acid, according to Homberg. Mem. Par. 1703.

Here it appears that the ſulphur is firſt dephlogiſticated, and then unites to the fixed air of the oil: it evidently can receive no pure air from it. It muſt be remembered, that if this experiment be not cautiouſly conducted, it is very dangerous.

Theſe facts leave no reaſonable doubt, but that fixed air is produced by the combuſtion of ſulphur, and becomes a conſtituent part of the vitriolic acid. The following tends to prove that ſulphur contains phlogiſton, which may alſo be eaſily inferred from the foregoing.

1ſt. Doctor Prieſtley converted oil of vitriol into ſulphur, by evaporating it to dryneſs under a receiver filled with inflammable air. 6 Pr. 22: but as this experiment may be explained otherwiſe, I lay no great ſtreſs upon it, though it is perfectly ſatisfactory to thoſe who do not receive the antiphlogiſtic theory.

2d. The ſame excellent philoſopher, by means of a burning glaſs, melted ſome iron in vitriolic air; ſulphur was immediately formed, part of which united to the iron, and rendered it brittle, and part ſublimed: the reſiduary air was partly fixed and partly inflammable air *. Here the vitriolic air was converted into ſulphur by the inflammable air of the iron, and the fixed air found was that which was expelled from the vitriolic air in the inſtant of

* 6 Pr. 116.

its converſion into ſulphur; ſo that this curious experiment demonſtrates both points of my theory. I am ſenſible the antiphlogiſtians will reply, that the inflammable air proceeds from the decompoſition of the water contained in the vitriolic air, and the fixed air from the plumbago of the iron; but not to anticipate what I ſhall hereafter urge againſt the decompoſition of water, I ſhall only ſay, that it is not poſſible to aſcribe the fixed air to the decompoſition of the plumbago; for Doctor Prieſtley's burning glaſs cannot melt above 20 grains of iron, and according to Mr. Bergman, 100 gr. of iron contain but 0,12 of a gr. of plumbago, and conſequently the whole 20 gr. contain but 0,024 of a gr. and of this only $\frac{1}{3}$ is fixed air, a quantity almoſt imperceptible.

3d. If the moſt dephlogiſticated calx of iron, and on that account perfectly inſoluble in dephlogiſticated nitrous acid, be made into a paſte with ſulphur and water, and ſlightly heated, it will become ſoluble in the nitrous acid, having taken phlogiſton from the ſulphur *. It cannot be ſaid that the ſulphur took part of the oxigenous principle from the iron; for by Mr. Lavoiſier's table, iron has far a greater affinity to that principle than ſulphur has.

4th. If ſulphur be incloſed in a heated earthen

* Stahl, 300 Obſerv. p. 352.

tube, and the vapour of water made to paſs through it, the ſulphur will be decompoſed, and inflammable air obtained *. It cannot be ſaid that the water was decompoſed; for, by Mr. Lavoiſier's table, the oxigenous principle has a ſtronger affinity to the inflammable than to ſulphur.

5th. It is allowed by the antiphlogiſtians, that volatile alkalis contain phlogiſton; now, if vitriolic ammoniac be ſublimed, part of it will be decompoſed, and the acid becomes ſulphureous †.

6th. Mr. Weſtrumb threw about a drachm of calcined magneſia into an ounce of concentrated black vitriolic acid; in an inſtant both heated, and a bright flame appeared; but with dephlogiſticated vitriolic acid, or ſtrong nitrous acid, this did not happen ‡. Here the vitriolic acid having a ſtrong affinity to the magneſia, and its phlogiſton a ſtrong affinity to the common air, a ſeparation and double union rapidly enſued, and hence the flame. But as the dephlogiſticated vitriolic acid contained no phlogiſton, flame could not be produced.

7th. If ſulphur be digeſted in the nitrous acid, it is gradually decompoſed; the nitrous acid becomes phlogiſticated, and is in great

* 6 Pr. 150. † Mem. Par. 1783, p. 736.
‡ Chy. Annals, 1784, p. 432.

meaſure

meaſure converted into nitrous air, while the greater part of the ſulphur is converted into vitriolic acid *. Now, nitrous acid cannot be converted into nitrous air, without the addition of phlogiſton, as will be ſeen in the next ſection.

The vitriolic acid, impregnated with nitrous air, has leſs affinity to water, and may ſubſiſt in a dry ſtate †.

* Chaptal p. and Cornette Mem. Par. 1779, p. 484.
† 4 Pr. p. 26.

NOTE

OF

MR. LAVOISIER

UPON THE

VITRIOLIC ACID.

ACCORDING to Mr. Kirwan, ſulphur is compoſed of a baſe or radical, which, when ſaturated with phlogiſton, or, which is the ſame thing, with inflammable gas or hydrogene, forms ſulphur; and when it is ſaturated with fixed air, or carbonic acid, forms the vitriolic or ſulphuric acid. But as the carbonic acid is compoſed, according to him, of oxigene and hydrogene, and as the hydrogene is already pre-exiſtant in the ſulphur, it muſt follow that nothing more is neceſſary than the addition of oxigene, to change ſulphur into vitriolic or ſulphuric acid. From this it is immediately ſeen, that Mr. Kirwan perfectly agrees with us in the principal fact, that he is forced to admit that the ſulphur enters wholly into the compoſition of the ſulphuric

phuric acid; that oxigene likewiſe enters into, and forms a conſtituent part of the acid; and, laſtly, that no other principles exiſt in the ſulphuric acid but ſulphur and oxigene. The only point which divides us is, that Mr. Kirwan refuſes to adhere, as we do, to the immediate conſequence of facts, and that he ſuppoſes that the oxigene, when it unites with ſulphur, meets the phlogiſton or hydrogene, which converts it into carbonic acid, and that this acid combines with the ſulphur to form ſulphuric acid.

Mr. Kirwan therefore has two things to eſtabliſh in ſupport of his ſyſtem; the firſt, that ſulphur contains inflammable or hydrogenous gas, which he has not yet proved; and the ſecond, that the union of hydrogene and oxigene forms fixed air, or carbonic acid. Now it is rigorouſly proved, on the contrary, that the carbonic acid is nothing elſe but the reſult of the diſſolution of charcoal in vital air or oxigenous gas. The aſſertion of Mr. Kirwan therefore includes a gratuitous ſuppoſition, and an error; and conſequently is inadmiſſible. I will ſay more; namely, that even if we admit Mr. Kirwan's data, the difficulties are encreaſed, inſtead of being removed, and that they do not explain any of the phenomena of the combuſtion of ſulphur.

In fact, how was it that Stahl was led to ſuppoſe that an inflammable principle exiſted in combuſtible bodies? It is becauſe he apprehended that there was no other way of

explaining the diſengagement of heat and light which takes place at the moment of combuſtion. It is to the ſeparation or emiſſion of the inflammable principle which was impriſoned in thoſe bodies, but is ſet at liberty in this proceſs, that he attributes the effect; but in the hypotheſis of Mr. Kirwan there is no diſengagement of the inflammable principle in the combuſtion of ſulphur: this principle, on the contrary, remains engaged in the combination to form fixed air; the phenomena of combuſtion cannot therefore be attributed to it, ſo that they remain abſolutely without explanation in the ſyſtem of Mr. Kirwan. What then does he gain by his ſuppoſition? Additional difficulties, and no aſſiſtance to remove them.

He objects, that if red precipitate of mercury be taken and combined with flowers of ſulphur, diſtillation by gentle heat converts the ſulphur into ſulphureous acid, with ſcarcely any combuſtion; whence he concludes that fixed air exiſts in the calx of mercury, and that it is this fixed air which prevents the combuſtion; but it is eaſy to ſee, that what Mr. Kirwan here offers as an objection againſt the antiphlogiſtic doctrine, is one of the ſtrongeſt proofs which can be brought in its favour. It is preciſely becauſe the vital air exiſts in the ſtate of oxigene in the red precipitate, and becauſe it is deprived of the greateſt part of the caloric and light neceſſary to give it the gaſeous ſtate, that it cannot furniſh more when

it

it is combined with ſulphur, and that conſequently it is no longer ſuſceptible of burning *. This experiment exhibits therefore merely the ſimple and quiet tranſition of oxigene from one body to another; it proves that this principle, at the degree of heat employed to effect the decompoſition, has more affinity with the ſulphur than with the mercury. Mr. Kirwan can draw no concluſion in favour of his doctrine, from the very ſmall portion of fixed air or carbonic acid he obtained in this experiment; it proves only that the red precipitate he made uſe of had not been well ſecured from the contact of the air; for it is known that this metallic oxide, as well as thoſe of lead and iron, has the property of abſorbing the carbonic acid when left expoſed to the air.

The anſwers to almoſt all the objections contained in the ſame articles, are obvious; and as Mr. Kirwan has himſelf pointed them out, I ſhall forbear the diſcuſſion of them: there is only one object, upon which I ſhall add a few reflections.

Mr. Kirwan affirms, that if very dephlogiſticated calx of iron, (that is to ſay, iron highly charged with oxigene,) and on that account perfectly inſoluble in the nitrous acid, be

* This argument proves too much; for if it were generally applicable, the nitrous ſalts, and thoſe into which the dephlogiſticated or ſuperoxigenated marine acid enters, ought not to detonate with ſulphur or other combuſtible bodies. —Note of the Engliſh Tranſlator.

taken, and if after having formed it into a paſte with ſulphur and water, it be ſlightly heated, the calx becomes ſoluble in nitrous acid, "it cannot be objected," ſays he, "that "the ſulphur took part of the oxigenous "principle from the iron; for by Mr. La-"voiſier's Table, iron has far a greater affinity "to that principle than ſulphur has."

It is eaſy to foreſee, from what I have before ſaid, the reply I ſhall make to this objection. It is known that iron is ſuſceptible of various degrees of calcination, or, to ſpeak more correctly, that the combination of iron with oxigene is ſuſceptible of various degrees of ſaturation. The firſt of theſe degrees is the martial ethiops, or black oxide of iron, which contains about 30 per cent. of oxigene; next comes ruſt, or the yellow or red oxide of iron, which contains 40 or 50 per cent: but the affinity of iron with oxigene is not the ſame at theſe different degrees of ſaturation; it attracts it much more ſtrongly in the ſtate of ethiops, and much leſs in the ſtate of ruſt. Hence it follows, that iron which has the property of taking from the concentrated and boiling vitriolic acid a ſufficient quantity of oxigene to become ethiops, has not force enough to rob it of a larger quantity. The point of equilibrium between ſulphur, iron, and oxigene, is therefore the ſulphureous acid and the ethiops; whence it follows, that if the yellow oxide of iron be combined with ſul-

phur,

phur, the latter muſt take a portion of oxigene from the iron, and revive it to the ſtate of black oxide or martial ethiops; that is to ſay, it brings it to the point of equilibrium. It muſt be recollected, that this point of equilibrium, as I have often obſerved already, varies according to the degrees of temperature. There is nothing in this which does not agree with all the known facts; and I have ſpoken beforehand concerning this difficulty, when I treated upon the inconveniences which attend the preſent form of our tables of affinities.

SECT.

SECT IV.

Of the Nitrous Acid.

THE important diſcovery of the ſubſtances which contribute to the artificial production of the nitrous acid, made by Mr. Cavendiſh, and of thoſe which nature employs, made by Mr. Thouvenel, together with the numerous and ingenious experiments contained in Dr. Prieſtley's laſt publication, have at laſt diſſipated moſt of the obſcurity attending its operations, and the nature of its modifications. Nor have the labours of the antiphlogiſtians been uſeleſs; both Mr. Lavoiſier and Berthollet, by carefully diſtinguiſhing the component parts, particularly of nitrous air, have thrown great light on the ſubject, though by neglecting one eſſential part, namely, the phlogiſton, they have obliged me to differ from them in ſome particulars. By theſe helps I am enabled to give a new, and to me at leaſt a more ſatisfactory theory of this ſingular acid than has yet appeared; and at the ſame time, to ſhew the weakneſs of the antiphlogiſtic doctrine.

Mr. Cavendiſh has ſhewn, that the nitrous acid may be formed by taking the electric ſpark in a mixture of 3 meaſures of phlogiſti-

cated

cated air, and 7 of dephlogiſticated air, or in weight, 1 part of the former, and about 2,6 of the latter.

According to Mr. Lavoiſier, nitrous acid conſiſts of nitrous air, as its *baſis*, united to the oxigenous principle. And 100 grains of *dry nitrous acid* conſiſts of 64 grains of *nitrous air*, united to 36 grains of *pure air* deprived of its ſpecific fire—that is, by meaſure, according to my calculation, 173 cubic inches of *nitrous air*, and 105 of *pure* air*.

But *nitrous air* itſelf, as he well remarked, is a compound; 100 grains of it, according to him, contain 32 of phlogiſticated, and 68 of *pure* air. And, conſequently, 64 grains of it contain 20,5 of phlogiſticated air, and 43,5 of pure air†. Hence, according to him, 100 grains of dry nitrous acid contain 79½ pure air, and 20½ phlogiſticated air.

This proportion of *pure* air and *phlogiſticated* air differs, as we ſee, very conſiderably from that of Mr. Cavendiſh; but, as Mr. Lavoiſier well remarks, the nitrous acid is not always in the ſame condition, the *red* ſort differing very conſiderably from the *pale and colourleſs*; the former contains more nitrous air, which may be ſeparated from it by mere heat, and, therefore, muſt contain more phlogiſticated air than the latter; and in fact, the nitrous acid produced

* Or in French meaſures 142.7 cubic inches of nitrous gas, and 86.5 of oxigenous gas.

† 11 Mem. Scav. Etrang. p. 629.

by

by Mr. Cavendiſh was of the red ſort, or that which we call highly phlogiſticated, and, conſequently, muſt have contained more phlogiſticated air than the pale or colourleſs. In my opinion 100 gr. of pure, dry, *colourleſs*, nitrous acid contain 38,17 gr. of *fixed air* as its acidifying principle, 57,06 of *nitrous baſis*, and 4,77 of phlogiſton united to the nitrous baſis. —As to the *nitrous baſis*, $\frac{1}{3}$ of its weight is phlogiſticated air, and $\frac{2}{3}$ dephlogiſticated or pure air, both in a concrete ſtate. It has an affinity both to fixed air, and to phlogiſton.

Nitrous baſis ſaturated with phlogiſton conſtitutes *nitrous air*: 100 gr. of this baſis take up nearly 22 of phlogiſton. The proofs of this theory will preſently be ſeen.

Hence the conſtituent principles of nitrous acid are fixed air, dephlogiſticated air, phlogiſticated air, and inflammable air, all in their concrete ſtate.

Red, *yellow*, *green*, and *blue* nitrous acids, when thoſe colours are intenſe, owe their origin to the abſorption of nitrous air, and, conſequently, the proportion of their principles are variable, though all have the dephlogiſticated acid for their ground. Thus Dr. Prieſtley having expoſed ſtrong pale yellow nitrous acid, (whoſe ſpecific gravity could not be leſs than 1,400) to nitrous air, found that 100 gr. of this acid abſorbed in 2 days 247 cubic inches of nitrous air*; now 100 gr. of this ſpirit of

* One hundred and twenty-two grains French would therefore abſorb 204,022 inches of nitrous gas.

nitrous

nitre muſt have contained, by my calculation, about 21 gr. of dry acid, and theſe 21 gr. took up 91,39 gr. of nitrous air. When about 20 cubic inches* of nitrous air were abſorbed (that is, about 7† gr.), the acid became of an *orange* colour; when 50 cubic‡ inches were abſorbed (about 18‖ gr.) it became *green*; and when nearly the whole was abſorbed, it evaporated in the form of nitrous vapour, carrying off part of the water with it§.

Hence we ſee that *nitrous vapour* conſiſts of nitrous acid, united to 3 or 4 times its weight of nitrous air, and a little water. This vapour is always of a *red* colour. We ſee alſo that the nitrous acid is phlogiſticated by abſorbing nitrous air. This red vapour muſt carefully be diſtinguiſhed from another colourleſs inviſible vapour, which Dr. Prieſtley often mentions, and which is nothing elſe but the nitrous acid itſelf diſengaged from water.

Nitrous air is ſeldom perfectly pure; it is ſubject to two contaminations, one from nitrous vapour, and the other from phlogiſticated air, whoſe origin I ſhall here explain: When a metal or any phlogiſticated ſubſtance is diſſolved in the nitrous acid, this ſubſtance attracts the acidifying principle of the nitrous acid, and its phlogiſton is attracted by the nitrous baſis; and thus by a double affinity the

* 16,92 French cubic inches. † 8,54 French grains.
‡ 41,30 French inches. ‖ 21,96 French grains.
§ 3. Pr. 123.

nitrous

nitrous acid is in part decompoſed, and nitrous air formed. Part of this nitrous air eſcapes out of the ſolution, but a part of it unites to the undecompoſed acid, particularly if this acid were dephlogiſticated, and with it forms nitrous vapour; of this nitrous vapour part unites to the metallic ſalt or calx, and part flies off mixed with the nitrous air, which it contaminates: from the union of the nitrous air with the undecompoſed acid and metallic calx, proceed the various colours which ſtrike the beholder during the ſolution of mercury in ſtrong nitrous acid. Again, when iron, and particularly zinc, tin, or regulus of antimony, are rapidly diſſolved in nitrous acid, as theſe ſubſtances give out their phlogiſton very copiouſly, or at leaſt very readily, not only the acidifying principle, or fixed air, unites to them; but the nitrous baſis itſelf, by reaſon of the heat generated, and the ſudden eruption of phlogiſton, is decompoſed, its pure air uniting to the phlogiſton, and forming fixed air, while the phlogiſticated air flies off, mixes with and contaminates the nitrous air.

The *nitrous baſis*, free from the acidifying principle and adventitious phlogiſton, forms that ſpecies of air which Dr. Prieſtley calls *dephlogiſticated nitrous air*, and to which I have given the name of *deacidified* nitrous air: both appellations conſidered in a proper view, are equally juſt; for when it is ſo pure as to admit a candle to burn with an enlarged flame, it is equally

equally free from the ſmall portion of phlogiſton which uſually adheres to it, and from nitrous vapour. The dephlogiſticated air it contains is ſo ſtrongly combined with the phlogiſticated air, that they cannot be ſeparated but in a red heat, or by a double affinity: and hence, though it admits a candle to burn more or leſs perfectly, as it is more or leſs pure, yet an animal cannot live in it. A ſure ſign that it generally contains a ſmall portion of phlogiſton, is its reddening with dephlogiſticated air; but it will not decompoſe nitrous air, becauſe its pure air is already united to phlogiſticated air. It may appear extraordinary that this air, which (ſince it is a part of the nitrous acid) is formed by the electric ſpark, ſhould alſo be decompoſed in a red heat; but it ſhould be remembered, that during its formation, the pure air meets with no phlogiſton but that contained in the phlogiſticated air, which is incapable of inflammation; but when the flame of a candle is preſented to it, it meets with uncombined phlogiſton, with which in that heat it can readily unite.

Having explained theſe modifications of the nitrous acid in a general way (for a detail of particulars would be much too prolix); it now remains for me to prove the preſence of phlogiſton in phlogiſticated air and in nitrous air, and alſo the exiſtence of fixed air in nitrous acid; in doing which it will appear that dephlogiſticated air and nitrous air ſhould not be

looked upon as its conſtituent principles: after which I ſhall examine the moſt remarkable experiments that have been made with this acid.

With reſpect to *phlogiſticated air*, it muſt be owned we have no direct proof that it contains phlogiſton, as no inflammable air has as yet been extracted from it, nor is it the general reſult of phlogiſtic proceſſes; but ſince the nitrous acid formed of this air and dephlogiſticated air, was found ſtrongly phlogiſticated, and ſince the phlogiſticated nitrous acid is conſtituted ſuch, by its union with nitrous air, it is evident that phlogiſticated air muſt contain phlogiſton, if nitrous air contains any.

That *nitrous air* contains phlogiſton, appears by the following experiments:

1ſt. The nitrous acid dephlogiſticates *ſulphur*, and in ſo doing, is converted in great meaſure into nitrous air; now it has been already proved that ſulphur contains phlogiſton: it alſo dephlogiſticates phoſphorus, ſugar, and metals, in which the preſence of that principle will hereafter be ſhewn.

2d. If the electric ſpark be taken in nitrous air, it will be reduced to $\frac{1}{3}$ of its bulk, and the reſiduum is mere phlogiſticated air *, and a little acid is depoſited. Now the antiphlogiſtians own that nitrous air contains both pure air and phlogiſticated air; ſince, therefore, this pure

* 6 Pr. 430, and 312 Van Marum, 27 Roz. 150.

air diſappears, is it not evident that it was converted into water? and ſince the formation of water requires the preſence of inflammable air, does it not follow that the nitrous air contained this alſo? and will not then the phlogiſticated air remain ſingle and alone? As to the acid depoſited, it evidently proceeds from the nitrous vapour almoſt always diſperſed through nitrous air.

Analogous to this, is the following experiment made by Dr. Prieſtley: If a few grains of iron be melted in nitrous air, the iron increaſes in weight, and nothing but phlogiſticated air remains*. Here the nitrous air is in the ſame manner decompoſed, the phlogiſton of the iron and its own uniting to the pure air, form water, which, uniting to the iron, increaſes its weight, and only the phlogiſticated air remains.

3d. Dr. Prieſtley having thrown the focus of a burning glaſs on nitrated lead, in a receiver filled with inflammable air, found the inflammable air to diſappear; the lead in great meaſure revived, and $\frac{2}{5}$ of the receiver filled with nitrous air; in this caſe, therefore, the inflammable air was taken up partly by the metal which it revived, and partly by the decompoſed nitrous acid, whoſe baſis is converted into nitrous air. The antiphlogiſtians will, probably, reply, that the acid was de-

* 6 Pr. 304.

compoſed, the inflammable air uniting to its oxigenous principle, and forming water, while the nitrous air was barely let looſe, and not formed. This anſwer ſuppoſes that nitrous air is a conſtituent principle of the nitrous acid, which we ſhall preſently prove to be falſe, and is indeed inconſiſtent with their own principles, for it would follow from thence that the nitrous acid ſhould be decompoſed, and nitrous air produced by boiling charcoal in this acid; ſince, by the antiphlogiſtic table, charcoal has far a greater affinity to the oxigenous principle than nitrous air has. Yet Mr. Lichtenſtein has lately ſhewn that charcoal rather retains than ſets looſe nitrous air*.

The following experiments ſhew that nitrous air is not a conſtituent principle of the nitrous acid, but that fixed air is; which is the 3d point that remained to be proved.

1ſt. There is not a doubt, but that pure nitrous acid enters intire, and without decompoſition into fixed alkalis, and forms nitre. Now if nitre be diſtilled in a good earthen retort, it will be wholly decompoſed, and ſo alſo will the acid itſelf, except a few drops which paſs in the beginning of the diſtillation†; and nothing but dephlogiſticated air more or leſs pure (and, conſequently, intermixed with

* Chy. Annal. 1786. p. 217.
† Mem. Par. 1781. p. 23.

phlogiſticated

phlogiſticated air), and a ſlight proportion of fixed air, will be found: theſe, therefore, are its true conſtituent parts, when diſengaged from ſubſtances that cannot communicate phlogiſton to it in any remarkable quantity, ſuch as alkalis and earths; but if it be ſeparated from ſubſtances that contain phlogiſton, ſuch as metals, it will then indeed be reſolved into nitrous air, and dephlogiſticated air more or leſs pure, the phlogiſton of the fixed air being detained by the metal. Theſe facts being of great conſequence towards underſtanding the compoſition of this acid, require to be more fully ſtated.

Mr. Berthollet, who ſeems to have made this experiment with moſt exactneſs, from 472,5 grs. troy*, of nitre, obtained 701,22 Engliſh cubic† inches of air, that is, at the rate of 714 from a troy ounce of nitre‡. This air is far from being of the pureſt kind, ſince the ſtandard of the greater part of it is 0,95, by Dr. Prieſtley's teſt, whereas that of the beſt is 0,03, therefore it contains phlogiſticated air. And both Dr. Prieſtley, Mr. Berthollet, and Mr. Succow, obſerved that the portion of air which firſt paſſes, contains fixed air, rendering lime-water turbid‖. Mr. Suc-

* Or 576 French grains, or one ounce.

† Or 580 French cubic inches.

‡ Mem. Par. 1781. p. 23.

‖ 4 Pr. 252. Mem. Par. ibid. 1 Chym. Annal. 1785. p. 104.

cow obſerved it alſo in the laſt portion of this air. Here, then, we have the three conſtituent parts of nitrous acid, with ſcarce any nitrous air, which the antiphlogiſtians ſuppoſe to be one of its conſtituent parts, and to make $\frac{2}{3}$ of the bulk of the acid, when exhibited in an aerial form.

However, a ſmall quantity of nitrous vapour is generally diffuſed through the air thus obtained, becauſe the acid, as well as the alkali, of which nitre is formed, are both ſomewhat phlogiſticated; the alkali being common potaſh, which is more or leſs in a ſaponaceous ſtate, or mixed with coal, and the acid as being generally extracted from calcareous earths, mixed with animal ſubſtances. In the beginning of the diſtillation, part of the acid paſſes undecompoſed, by favour of the water of cryſtallization.

It may be ſaid with great appearance of truth, that the proportion of fixed air, thus obtained, is too ſmall to deſerve to be ranked among the conſtituent parts of the nitrous acid. Before I anſwer this objection, it will be proper to determine in what proportion it ſhould be contained in this acid; this proportion, as we have already ſeen, is variable, the phlogiſticated acid containing leaſt, and the dephlogiſticated moſt; but, in general, we may rate it at $\frac{1}{3}$ of the acid, as exiſting in nitre. When the nitre is expoſed to a red heat, the union of the conſtituent parts of the acid

acid is gradually broken; that part of the acid which is at the ſurface of the alkali, being in contact with the water, which is the moſt volatile ingredient, is not ſo ſtrongly acted upon by heat, but paſſes undecompoſed. The reſiduary nitrous acid becoming now more and more concentrated, decompoſes its own fixed air, and thereby becomes more and more phlogiſticated*. This phlogiſtication continues to the laſt, the retained part always dephlogiſticating that which eſcapes, until it is itſelf at laſt forced out; and hence the laſt portion is the moſt impure, and even contains nitrous air.

That fixed air may be decompoſed in this manner, appears from ſundry other experiments; for inſtance, that in which Dr. Prieſtley obtained dephlogiſticated air from acetous ſelenite, 6 Pr. 292, and alſo, that in which both he and Mr. Laſſone obtained air nearly of the goodneſs of common air, from limeſtone, after the greater part of the fixed air had paſſed. 6 Pr. 227.

To make this matter ſtill more intelligible, it muſt be obſerved, that if nitre be heated ever ſo long, yet if we examine it at any period before its total decompoſition, no part of the acid will be found phlogiſticated, but that

* Of this phlogiſtication of the nitrous acid, by re-action on itſelf, we have a full proof, in the red colour which it aſſumes when heated in glaſs tubes, hermetically ſealed. 3 Pr. 187.

near the ſurface, which, in the inſtant of its extrication, is dephlogiſticated by the portion of the acid next under it, which then becomes phlogiſticated, and is in the ſame manner decompoſed in its turn, by the next inferior ſtratum; and this proceſs continues until the whole is decompoſed. This I have found, by pouring nitrous acid on melted nitre, which never expelled any more than a ſmall portion of nitrous vapour; hence, Mr. Berthollet imagined that Mr. Bergman was deceived, in aſſerting that phlogiſticated nitre might be decompoſed by the acetous acid; for, in effect, it can decompoſe but a ſmall part of it, as only a ſmall part of any portion of melted nitre is really phlogiſticated; even dephlogiſticated air from red precipitate, contains a portion of fixed air, as Dr. Prieſtley, Mr. Lavoiſier, and Mr. Monge have obſerved*.

2d. Mr. Berthollet diſtilled 472,5 grs.† of nitre with ½ that weight of filings of iron, and obtained 453,37 Engliſh cubic‡ inches of air, nearly of the ſame goodneſs as common air, that is, containing a mixture of pure, and phlogiſticated air, and not a particle of nitrous air; but the alkaline maſs that remained, contained fixed air‖. It were abſurd to attribute this fixed air to the plumbago of the iron, of which Mr. Bergman ſays, *ferrum ductile fere nihil plumbaginis fovet*§. But it may, in

* 2 Pr. 217. Mem. Par. An. 1782, p. 495, and 1783, p. 85. † One ounce. ‡ 374,48 French inches.
‖ Mem. Par. 1781, p. 234. § 3 Bergm. 49.

this

this caſe, come either from the decompoſition of the nitrous acid, or from the union of the phlogiſton of the iron, with the dephlogiſticated air of the nitre, but moſt probably from both. When equal weights of nitre and filings of iron were uſed, ſtill there was not a particle of nitrous air; becauſe, in effect, the iron was not attacked by the undecompoſed nitrous acid, but there was a greater mixture of phlogiſticated air, becauſe the nitre was, by reaſon of the preſence of iron, decompoſed by a more moderate heat, and the alkali, for the ſame reaſon, contained ſtill more fixed air than in the former caſe.

The ſame experiment ſucceeded in the ſame manner with Mr. Achard*; he found fixed air not only in the alkalized nitre, but alſo in the air that eſcaped, having probably uſed a greater heat, by which more fixed air was produced than the alkali could retain in that heat. Mr. Berthollet found a mixture of 120 grains of nitre, and 60 of zinc, to produce ſo much fixed air, during detonation, as to precipitate 3 or 4 quarts of lime-water; he alſo found a mixture of nitre and copper to produce fixed air, though they ſcarcely detonated, as copper difficultly parts with its phlogiſton. Mr. Cavallo found a mixture of 3 parts nitre, 1 of ſulphur, and 1 of copper, to afford fixed air, and phlogiſticated air; the fixed air was $\frac{1}{10}$ of the whole†. Hence

* Chy. Annal. 1784. p. 493.
† Cavallo on Air, p. 815.

I think

I think it evidently follows, that fixed air is a conſtituent part of the nitrous acid; yet I have often thrown nitre on red hot filings of iron, and always found the alkali cauſtic, the reaſon of which may be, either that water, and not fixed air, is produced in a red heat, or that the dry alkali could not retain the fixed air in ſo high a heat.

Sixty grs. of nitre, and 3 of charcoal, diſtilled, produce fixed air and phlogiſticated air; 60 grs. of nitre and 6 of charcoal, ſlightly detonated, and produced alſo fixed air, and more of phlogiſticated air, but no nitrous air *; here the fixed air is partly an educt, and partly a product. The quantity of phlogiſticated air is greater, when more charcoal is uſed, becauſe the nitrous acid is decompoſed in a more moderate heat, and the phlogiſticated air it contains is not decompoſed; for I do not eſteem it a product of the operation. But as the nitrous acid is decompoſed before it unites with the charcoal, no nitrous air can be formed.

But the reſult is very different, when nitre is diſtilled with a ſmall proportion of ſulphur †: here nitrous air is the principal product, and a ſmall portion of dephlogiſticated air, which, being immediately converted into nitrous acid, by contact with a ſmall portion of the nitrous air, cannot be had ſeparate, but ſubſiſts in a ſtate of vapour, in the remainder of the nitrous air.

* Mem. Par. 1781, p. 231. † Ibid.

The

The reaſon why nitrous air is produced in this caſe is (as will be ſhewn more fully further on,) that part of the ſulphur being inflamed in the beginning, and converted into vitriolic acid, this acid re-acts on the nitre, and expels its acid without decompoſition; but the expelled acid meeting the uninflamed ſulphur, is immediately decompoſed by it, and robbed of its fixed air, at the ſame time that it robs the baſis of the ſulphur of its phlogiſton, and is thereby converted into nitrous air. The vitriolic acid, thus formed of the fixed air of the nitrous acid, and of the baſis of the ſulphur, expels more nitrous acid, which is decompoſed in the ſame manner, until the nitre is converted into tartar vitriolate: towards the end, a ſmall part of the nitre is decompoſed by heat alone, and hence the dephlogiſticated air ariſes.

If mercury, &c. be diſſolved in nitrous acid, and the ſolution diſtilled to dryneſs, nitrous air will be produced in the beginning, and at the laſt dephlogiſticated air. The nitrous air is here formed of the union of the phlogiſton of the metal with the nitrous baſis, while the fixed air unites to the metallic calx: at the end the fixed air is decompoſed, its dephlogiſticated part ſet looſe, while its phlogiſton revives the metal, as will preſently be ſeen more at large.

3. If ſpirit of nitre be made to boil, and its vapour received through a red hot earthen tube, it will be converted into dephlogiſticated air, in which a portion both of phlogiſticated

and

and fixed air is found, as Dr. Prieſtley has diſcovered: the water through which this air paſſes will contain alſo fixed air.

Here then are ſeveral ways of decompoſing the nitrous acid, and in one only it is reſolved into nitrous and dephlogiſticated air, and in this way it may, at leaſt, be ſtrongly ſuſpected to receive an addition of another principle; why then ſhould theſe be regarded as its conſtituent principle? and as in the two ſimpleſt methods of decompoſition, in which the re-action of no foreign ſubſtance can be ſuſpected, it appears in the form of dephlogiſticated, phlogiſticated, and fixed air (the former always containing a mixture of the two laſt,) why ſhould not theſe be accounted its true conſtituent parts?

4. This theory is further confirmed by reflecting on the manner in which nitrous acid is generated by nature. Mr. Thouvenel* found that this acid is conſtantly produced when chalk is expoſed to a mixture of putrid air and common air, or putrid air and dephlogiſticated air; but if the putrid air be paſſed through lime-water, it is never generated, and that it is rarely produced by expoſure of quicklime, or fixed alkalis, to theſe airs. Does not this experiment imply that fixed air is an eſſential ingredient in this production? The reaſon that alkalis, though aerated, are not ſo proper, is, that they do not combine with

* 11 Sçav. Etrang. p. 126. 128.

phlogiſticated

phlogiſticated air, as calcareous earths do. Mr. Cavendiſh, indeed, produced nitrous acid, without any apparent mixture of fixed air; but the atom of fixed air, neceſſary for the formation of the ſmall quantity of nitrous acid he produced (about $\frac{1}{3}$ of a grain,) might well be contained in the phlogiſticated air he uſed, or perhaps formed in the operation; for it is impoſſible to deny all credit to thoſe who aſſerted that lime-water was precipitated by taking the electric ſpark in common air, though it did not ſucceed with him, either from his uſing an inſtrument of different power from that uſed by others, or air phlogiſticated by a different proceſs.

5. Having diſſolved, or rather calcined, 371 gr. of clean iron filings in 1451 gr. of red nitrous acid, whoſe ſpecific gravity was 1,456, which I ſlightly diluted, and let the nitrous air eſcape, I diſtilled the ſolution with a gradual heat until the retort was perfectly red hot, and received the air over mercury, having an apparatus for receiving the acid liquor apart. After ſome common and nitrous air had paſſed, I obtained air ſomewhat worſe than common, in 4 portions, each portion containing fixed air; the next day adding more water, I obtained ſtill more fixed air as long as any liquor remained.

6. Dr. Prieſtley having diſtilled a quantity of iron filings, converted into perfect ruſt by long expoſure to nitrous air, obtained from them

them a large quantity of air, the far greater part of which was fixed air, mixed with a little phlogiſticated air, and at laſt pure air. 6 Pr. 319. The fixed air here proceeded for the moſt part from the decompoſition of the nitrous air, its dephlogiſticated part taking phlogiſton from the iron.

I ſhall now examine the explanation of theſe phænomena given by other philoſophers, and particularly by the antiphlogiſtians.

My ingenious friend Mr. Watt, and alſo Mr. Cavendiſh*, are of opinion, that the whole quantity of dephlogiſticated air, produced from the diſtillation of nitre, ariſes from the dephlogiſtication of the water it contains, it being decompoſed by the nitrous acid which then becomes phlogiſticated. This opinion is expoſed to inſurmountable difficulties; for in the firſt place, nitre affords dephlogiſticated air at the rate of 146,125 † cubic inches for every hundred ‡ grains of nitre; and ſuppoſing 100 cubic inches of dephlogiſticated air to weigh but 32 gr ‖. which is the loweſt computation, and may be allowed on account of the mixture of phlogiſticated air, 146,125 cubic inches ſhould weigh 46,77 § gr. but then dephlogiſticated air is only one of the conſtituent parts of water; for it contains 13 per cent. of inflammable air, that is to ſay, 87 gr.

* Phil. Tranſ. 1784, p. 144 and 337.

† 120.699 French inches. ‡ 122 grains French.

‖ 45.29 grains French. § 66.216 grains French.

of

of dephlogiſticated air: to form 100 gr. of water requires an addition of 13 gr. of inflammable air, conſequently 46,77 gr. of dephlogiſticated air require nearly 7 of inflammable air, and would then form 53,77 gr. of water, which exceeds half the weight of the nitre, as Mr. Watt candidly owns, which quantity of water is certainly inadmiſſible; for it evidently contains at leaſt $\frac{1}{2}$ its weight of alkali, and then no room would be left for the acid; beſides, the phlogiſticated air cannot be derived from the water, and it makes up about $\frac{1}{3}$ of the whole, ſo that of neceſſity the acid muſt be decompoſed: beſides, no ſatisfactory account is given of what becomes of the acid. Mr. Watt found that the water over which the air proceeding from the decompoſition of 960 gr. of nitre, had been received, contained only the acid belonging to 120 gr. of nitre, and even this ſmall quantity he inferred only from my experiments; but my experiments are totally inapplicable in this caſe, for I uſed only the dephlogiſticated nitrous acid, and alkalis are ſaturable by a much ſmaller quantity of phlogiſticated than of dephlogiſticated acids, as is evident in the caſe of the dephlogiſticated marine acid, as Stahl long ago obſerved; for he ſays that the volatile acid of ſulphur ſaturates 10 times as much alkali as the fixed*. Mr. Bergman and alſo Scheele

* See his Treatiſe on Salts, p. 160 of the French edition.

obſerved,

obſerved, that melted nitre is ſtill neutral, though it is phlogiſticated; therefore it is air, and not water, which it wants; accordingly Dr. Prieſtley found it to injure common air, by attracting its dephlogiſticated part: but if it be kept ſome time in fuſion, it loſes its acid, and becomes alkaline, and the air it recovers muſt ſurely be deemed rather to recompoſe the acid than to form water, of whoſe formation in the temperature of the atmoſphere we have no ſort of proof. On the contrary, the impoſſibility of accounting for the loſs of acid in this caſe, is an evident proof of the fallacy of that hypotheſis.

By Mr. Lavoiſier's analyſis* 100 gr. of nitre contain 57 of cauſtic alkali; by Mr. Bergman's, 49; by Mr. Wenzel's, 52; by Mr. Wiegleb's, 46½; by mine 63; the mean of all which is 53½, which leaves 46,5, for acid and water, which is very nearly the weight of the air expelled. The different quantity of acid aſſigned by different perſons to nitre, is, in part, owing to its degree of phlogiſtication in nitre†. I believe at preſent that 100 gr. of nitre contain 34 of acid, and about 12 of water, including the water in the acid, and that of cryſtalization.

The antiphlogiſtians have as yet given no explanation of the decompoſition of nitre by heat.

* 11 Sçav. Etrang. 627. † For of the dephlogiſticated acid, as it becomes phlogiſticated in uniting to the alkali, leſs is required.

The

The detonation of nitre with charcoal was well executed, and the different aerial products well diſcriminated, though in my opinion not ſo well explained by Mr. Lavoiſier*.

Having reduced to a ſubtil powder, and well mixed together, 708,6 gr. of nitre and 93,52 of charcoal, he preſſed them into a copper tube; and after inflammation, plunged the tube, with its aperture turned down, under a jar of water, where it remained until the whole of the charcoal was conſumed, and the nitre decompoſed. The products were as follows †:

Materials.	Gr.	Products.	Cub. Inches.	Weight. Gr.
Nitre	708,6	Fixed air -	708,25 -	329,33
Charcoal	93,52	Phlog. air -	195,56 -	59,8
		Cauſtic alkali - - -		406,5
	802,12			
		Total of the products -		795,63
		Loſs — —		6,49

Mr. Lavoiſier thinks that the whole of the air of the nitre, except the 59,8 ‡ cubic inches

* 11 Mem. Sçav. Etrang. p. 626. Here, as in moſt other places, the French weights and meaſures are converted into Engliſh.

† In French numbers,

Materials.	Gr.	Products.	Cub. Inches.	Weight. Gr.
Nitre	864,592	Fixed air -	585,0145	401,782
Charcoal	114,094	Phlog. air -	161,532	72,956
		Cauſtic alkali - - - -		495,93
	978,686			
		Total of the products -		970,668
		Loſs — —		8,018

‡ 49,394 French inches.

of phlogiſticated air, united to the charcoal, and with it formed the fixed air; and yet we find a deficiency of 6,49 gr.* which does not appear in his account, becauſe he eſtimated the weight of the fixed air too high. I ſhall not at preſent examine whether charcoal in ſpecie unites to pure air, and forms fixed air, as that matter will be amply diſcuſſed in another ſection.

In my theory this experiment may be explained as follows: In the firſt place 708,6 gr. of nitre contains 240,9 gr. of real acid: of this 59,8 gr. (allowing ſome water contained in this air) are phlogiſticated air; the remainder 181,1 gr. are dephlogiſticated air, or, which is the ſame in effect, pure air mixed with fixed air. This air, if totally pure, would take from the charcoal 37 gr. of phlogiſton, and then form 218,1 gr. of fixed air, to which adding the fixed air in the charcoal itſelf, we have 274,62 gr. of fixed air, and adding to this $\frac{1}{5}$ of its weight of water, we ſhall have 329,62 gr. of fixed air. The particulars may be ſeen in the following detail.

	Gr.
Total weight of the air expelled from nitre -	240,9
Subtract for phlogiſticated air -	59,8
Dephlogiſticated air from nitre -	181,1
Add to this inflammable air from the charcoal	37
Fixed air formed -	218,1

* 8.018 French grains.

Reſiduum

Reſiduum of the charcoal, being fixed air 93,52—37=56,52
Total fixed air=218,1+56,52=274,62
Add $\frac{1}{5}$ of its weight of water=55

Total weight of fixed air	329,62
Weight of phlogiſticated air	59,8
Cauſtic alkali - - -	406,5
	795,92

This experiment, though not altogether exact, as the quantity of water in different airs has not as yet been exactly determined, has great merit. Mr. Lavoiſier has judiciouſly inferred from it that nitrous acid contains about $\frac{1}{5}$ of its weight of phlogiſticated air, even before Mr. Cavendiſh's diſcovery. It muſt alſo be allowed to be a complete proof of the formation of fixed air from dephlogiſticated and inflammable air, by all thoſe that believe charcoal to be a compound; for the whole of the fixed air here found could not by any poſſibility exiſt in the charcoal, it being more than triple its weight. We may alſo infer from it, that phlogiſticated air may be decompoſed and burnt during the diſtillation of nitre *per ſe*, for the reſulting air never contains $\frac{1}{5}$ of phlogiſticated air.

The detonation of nitre with ſulphur, has alſo been well obſerved by Mr. Berthollet. He found that if nitre and ſulphur be well mixed in the proportion of 2 of the former to 1 of the latter, there is always a detonation; but if the proportion of ſulphur be to that of

nitre, as 1 to 4, the nitre is decompoſed without detonation, and nitrous air is produced. Thus he found that 30 gr. of ſulphur diſtilled with 120 of nitre, produced 108,8 cubic inches * of nitrous air, that is 40,27 gr.† and the nitre was totally decompoſed. This experiment is thus explained in my principles:

100 gr. of nitre contain about 46 of acid, comprehending the water which always accompanies it, and which cannot be ſeparated; therefore 120 gr. of nitre contain 55 of acid. $\frac{2}{3}$ of the nitrous acid in nitre is nitrous baſis. Now the $\frac{2}{3}$ of 55 is 36,6, therefore in this caſe we have 36,6 of nitrous baſis.

But nitrous air conſiſts of nitrous baſis united to 0,18 of its weight of phlogiſton. Now 0,18 of 36,6 is 6,6, then 36,6 + 6,6 = 43,2, then 43,2 ſhould be the quantity of nitrous air.

Again, $\frac{1}{3}$ of the nitrous acid in nitre is fixed air; therefore, 55 gr. of this acid ſhould contain 18 of fixed air, which it imparts to the ſulphur at the ſame time that it robs it of 6,6 gr. of phlogiſton; but 18 gr. of fixed air are far too little to convert 23,34 gr. of ſulphur, or rather of dephlogiſticated ſulphur into fixed vitriolic acid: it converts it therefore into vitriolic air, and ſaturates the alkaline baſis of the nitre.

In this caſe, therefore, there not being more phlogiſton than is neceſſary for the converſion

* 72,12 French inches. † 49,219 French grains.

of

of the acids into nitrous air and vitriolic air, a gradual production of these airs ensue in the manner explained p. 90.

But if a greater proportion of sulphur be used, then the nitrous basis itself is decomposed, meeting with a larger proportion of phlogiston, and hence scarce any nitrous air is found, but only phlogisticated, dephlogisticated, and vitriolic air; and as a larger quantity of air is suddenly let loose in a confined situation, a slight detonation necessarily ensues.

This experiment shews that nitrous air does not consist of nitrous acid, to which phlogiston is superadded, as Mr. Cavendish and I myself formerly thought. According to Mr. Cavendish, 87,5 gr*. of nitre contain the acid of 98,53 cubic inches† of nitrous air, and consequently 120 should contain the acid of 134 cubic inches‡ of nitrous air: yet in this experiment, though the nitre was totally decomposed, only 108,8 § cubic inches of nitrous air are produced. It is evident, therefore, that the nitrous acid loses one of its constituent parts when it acquires the phlogiston that converts it into nitrous air, and acquires that same constituent part, when, by the addition of pure air, nitrous air is converted into nitrous acid; therefore the phlogiston and pure air are not merely converted into water.

* 106, 75 French grains. † 81,385 French inches. ‡ 91,48. § 72,02.

33470

Before I enter on an explanation of Mr. Lavoiſier's experiments on the decompoſition of the nitrous acid by mercury, it will be neceſſary to explain ſome particulars relative to the formation of nitrous acid, from nitrous air and dephlogiſticated air.

When 1 meaſure of what is generally called very pure dephlogiſticated air, is carefully mixed with 2 meaſures of good nitrous air, they unite ſo perfectly, that only 0,27 of a meaſure remains: 1 meaſure of dephlogiſticated air, therefore, takes up 1,73 of nitrous air, but moſt commonly only 1,7. Yet in one caſe Dr. Prieſtley found both airs ſo pure, and mixed them ſo ſkilfully, that only ,03 of a meaſure remained; therefore, we may well ſuppoſe, that if both airs were perfectly pure and properly mixed, *nothing* would remain unabſorbed, and conſequently that 200 cubic inches of nitrous air would abſorb 100 cubic inches of dephlogiſticated air: however they unite, they always unite in this proportion, and the acid, thus formed, has all the pure air it is capable of taking up, and is what is called dephlogiſticated nitrous acid.

Hence 200 cubic inches* of nitrous air require for their thorough ſaturation 100 cubic

* In French meaſure 165,2 cubic inches of nitrous gas require for their ſaturation 82,6 cubic inches of oxigenous gas; and ſince the weight of the former is 87,54 grains, and that of the latter 41,48, the weight of the reſulting nitrous acid is 131,79 grains. And as 93,173 cubic inches of oxigenous gas abſorb 9,93 gr. of phlogiſton, 100 cubic inches of it ſhould take 7,216 of phlogiſton.

inches

inches of dephlogiſticated air; and ſince the weight of that quantity of the former is 74 gr. and of the latter 34, the weight of the reſulting acid is 108 gr. And as 112,8 cubic inches of dephlogiſticated air take 8,14 gr. of phlogiſton*, 100 cubic inches of it ſhould take 7,216 of phlogiſton.

Now 100 cubic inches of dephlogiſticated air=34 gr. to which adding 7,216 of phlogiſton, we have 41,216 of fixed air in 108 of dephlogiſticated nitrous acid: and if 108 of ſuch acid contain 41,216, 100 gr. of this acid will contain 38,16 of fixed air†. But it is ſeldom that given quantities of nitrous air and dephlogiſticated air unite ſo completely; for as ſoon as any part of the nitrous acid is formed by the union of the two airs, ſome part of the nitrous air unites to the newly formed acid, and ſome part of the dephlogiſticated air remains unſaturated: hence if the two airs do not immediately come into full and perfect contact, the diminution is not ſo great as it ſhould be, in proportion of the purity of both airs. Hence the acid thus formed is more or leſs phlogiſticated according to the quantity of unſaturated nitrous air combined with it, and this is a great ſource of uncertainty in eudiometrical experiments.

* See p. 20. and Phil. Tranſ. theſe 112,8 enter into 100 cubic inches of fixed air.

† In French meaſure, 72,6 cubic inches of oxigenous gas=41,48 grains, which with 8,803=50,283, of fixed air in 131,73 grains of nitric acid; and if 113,76 of this acid contain 50,283 of fixed air, 100 grains of the ſame acid will contain 38,16.

From what has been ſaid, we may ſee that even dephlogiſticated nitrous acid contains ſome phlogiſton, independent of that which is contained in the fixed air and phlogiſticated air, which are its conſtituent parts: for 200 cubic inches of nitrous air contain 13,4 of phlogiſton, and 100 cubic inches of dephlogiſticated air deprives theſe of only 7,216 gr. of this phlogiſton; therefore 6,184 ſtill remain in 108 gr. of this acid, and conſequently 100 gr. of the acid retain 5,72 of phlogiſton*, ſtill united to the nitrous baſis. By acid I always mean the dry acid, or at leaſt that which contains no more water than the air of which it was formed.

I now proceed to the celebrated experiment of Mr. Lavoiſier, which firſt gave riſe to the antiphlogiſtic theory, and on which it is ſtill chiefly founded.

To 945 gr. of nitrous acid, whoſe ſpecific gravity was 1,316, Mr. Lavoiſier added 1104 gr. of mercury†. Nitrous air was produced to the amount of 273,234 cubic inches; heat being applied, and the mercurial ſalt diſtilled to dryneſs, when it became red, dephlogiſticated air appeared, and continued until almoſt

* In French meaſure 165,2 cubic inches of nitrous gas contain 16,34 grains of phlogiſton, and 82,6 cubic inches of oxigenous gas deprives theſe of 8,803 grains; therefore 7,544 grains ſtill remain in 131,76 gr. of this acid; and conſequently 100 gr. of the acid retain 5,72 of phlogiſton.

† Mem. Par. 1776, p. 673.

the whole of the mercury was revived: it amounted to 287;742 cubic inches*.

Hence Mr. Lavoiſier concluded, 1ſt. That the nitrous acid was totally decompoſed, ſince it was reſolved into 2 ſpecies of air, by the reunion of which it might again be recompoſed, and conſequently that the weight of theſe two airs gives the weight of *real* acid contained in 945 gr. of ſpirit of nitre, whoſe ſpecific gravity is 1,316: 2dly. That ſince the mercury was recovered without any loſs or alteration, there is no reaſon to ſuppoſe that it loſt any thing during its ſolution in the acid, but that it was reduced to a calx merely by its union with pure air, ſince in proportion as this pure air was expelled, it recovered its metallic form.

To juſtify the *firſt concluſion*, three points ſhould have been proved; 1ſt. That during the diſtillation no part of the nitrous acid had eſcaped into the water over which the airs were diſtilled: 2dly. That the nitrous air produced during the ſolution, was not produced at the expence of ſome conſtituent part of the mercury, eſpecially as this was the point conteſted: 3dly. That by the reunion of the two airs, the ſame quantity of acid might be reproduced, which might eaſily be ſhewn by

* 1152 French grains of nitrous acid of the ſp. gr. of 1,316 and 1224 gr. of mercury, produced 225,691 cubic inches of nitrous gas and 217,694 cubic inches of oxigenous gas.

its

its again diſſolving the ſame weight of mercury; and if this were done, the firſt point would be ſufficiently clear.

Each of theſe points is ſo far from being proved, that it is clearly contradicted by experiment. To ſay nothing of my own experiments, nor of thoſe of Mr. Watt*, Mr. Lavoiſier himſelf found that a part of the acid always paſſes undecompoſed during the diſtillation of a ſolution of mercury†: 2dly. Nitrous air does contain one of the conſtituent parts of mercury, ſince the nitrous acid never affords nitrous air, but when it is diſtilled from a ſubſtance that contains the ſame conſtituent part that is attributed to mercury, namely the inflammable principle. Thus nitrous acid treated with ſpirit of wine, oils, or reſins, which the antiphlogiſtians allow to contain inflammable air, affords nitrous air, accompanied with other ſorts of air produced from thoſe ſubſtances‡; but diſtilled from alkalis, or earths, it yields none: 3dly. Not only the quantity of acid really decompoſed, cannot be reſtored by the union of the two airs obtained, but there is a large exceſs of one of them, which cannot be accounted for in the antiphlogiſtic hypotheſis; for the nitrous air obtained amounted to 273,234 cubic inches, or 101,09 gr. and the dephlogiſticated

* Phil. Tranſ. 1784, p. 339. † Mem. Par. 1782, p. 495. ‡ 2 Pr. 126, &c.

air

air to 287,742 cubic inches, or 97,83 gr. and the ſum of the weights of both airs ariſing from the decompoſed acid was 198,92 gr. Now if we mix both theſe airs together, they will unite, according to Mr. Lavoiſier (and this is the moſt favourable ſuppoſition) in the proportion of 69 of nitrous to 40 cubic inches of dephlogiſticated air*. Then as 69: 40 : : 273,234 : 143,8 : therefore 144 cubic inches, at moſt, of dephlogiſticated air will be taken up, the weight of which is 48,96, or 49 gr. conſequently the quantity of *reſtored acid* is almoſt 101,09+49=150,09 gr. though the weight of both airs be 198,92 gr†.

198,92
150,09

Deficit 48,83, that is, above $\frac{1}{4}$ of the whole.

Again, if from the whole quantity of dephlogiſticated air produced (that is 287,74 cubic inches) we ſubtract the quantity which

* Mem. Par. 1782, p. 488.

† In French meaſure 225,691 cubic inches, or 113,329 gr. of nitrous gas, and 217,674 cubic inches, or 119,35 gr. of oxigenous gas=together to 242,679 grains. And as in the mixture 69 parts of nitrous gas are required to 40 of oxigenous gas, it will follow that 69: 40 : : 225,691 : 118, 776; therefore 119 cubic inches at moſt of oxigenous gas, weighing 59,72, will be abſorbed: conſequently the quantity of reſtored acid is 123,329+59,72=183,046 gr. though the weight of the two airs be 242,679, whence the deficit is 59,630.

enters

enters into union with the nitrous air, we ſhall find an exceſs of 143,742 cubic inches, which is about $\frac{1}{2}$ of the whole. This half muſt, according to Mr. Lavoiſier himſelf, have exiſted in the nitrous acid, united to ſomething elſe, which is now miſſing. I aſk to what? nor do I ſee what can be reaſonably anſwered: the nitrous acid has therefore loſt ſomething, which this new hypotheſis does not account for.

It is true, Mr. Lavoiſier makes two attempts to obviate this objection. In the Memoirs of the Academy for 1776, he ſays this ſpirit of nitre was extracted by means of clay, and that ſuch acid always contains an exceſs of pure air; but can a principle actually combined with the nitrous acid, and which, ſo far from weakening, ſtrengthens and increaſes its acid properties, be called an exceſs? His ſecond attempt is to be found in the Memoirs of 1782: here he aſſerts, contrary to all experience, that nitrous acid conſiſts of equal parts by weight, of nitrous air and pure air, and by ſo doing, gives up the ſeeming advantage he had, by recompoſing the nitrous acid from both airs, for equal weights of both can by no art be brought to unite.

To ground the *ſecond concluſion*, Mr. Lavoiſier ſhould ſhew that mercury, during its revivification, took nothing from the ſubſtance to which it was united while a calx, of which ſubſtance the pure air might have been a component

ponent part: this cannot be ſhewn by ſtating the equality of weight of the calx, with that of the mercury and air together; for ſuppoſing the mercurial calx to have weighed 100 gr. the revived calx 90, and the air produced 10 gr. we ſhould then have 100 = 90 + 10, and in this way Mr. Lavoiſier would have the matter underſtood: but the ſame equality will be found, if we ſuppoſe the mercurial part of the calx, before its revivification, to weigh 89 gr. and the aerial part to weigh 11 gr. and that during the revivification, the calx attracts 1 gr. from the aerial part, for then the products will be equally 90 + 10. It is true, negatives in general need not be proved; but here there is a ſtrong preſumption that the aerial part has really loſt ſomething during its production, ſince it is incapable of forming a part of the ſame acid with which it was before combined; not, as happens in other caſes, by reaſon of its ſpecific heat, ſince a part of it will enter into ſuch combination, but for want of ſome other ingredient, which is loſt, and given up to the metal; and we may rather ſay there is a defect of nitrous air, than an exceſs of pure air.

The moſt reaſonable account of the above experiment ſeems to me to be the following.

945 gr. of ſpirit of nitre, whoſe ſpecific gravity is 1,316, contain by my table 219 gr. of real acid.

The

The weight of the acid actually combined with the mercury during the ſolution, muſt agree with that of the airs obtained; for though the phlogiſton of the nitrous air was taken from the metal, and therefore foreign to the acid; yet as the metal was at laſt revived, it muſt have taken from the acid as much phlogiſton as it gave to it: the weight of both the airs obtained amounts to 198,92 gr. therefore only about 200 gr. of the acid were decompoſed, and 19 gr. muſt have paſſed over during the diſtillation, as Mr. Watt alſo found; and, in fact, I found that 22 gr. of real acid diſſolve with the aſſiſtance of heat 100 gr. of mercury, and conſequently in this caſe, only 900 gr. of mercury were diſſolved, and 104 remained undiſſolved, which might well eſcape notice*.

The nitrous air we have already ſeen to amount to 101,09 gr. and the dephlogiſticated to 97,83; this quantity of nitrous air contains 18,18 gr. of phlogiſton, and conſequently 82,91 gr. of nitrous baſis.

Let us now examine the proportion and quantity of the conſtituent parts of the 200 gr. of acid that were decompoſed. I ſay 200, to avoid fractions, as 198,92 approaches very nearly to that quantity.

This acid, according to Mr. Lavoiſier's expreſſion, contained an exceſs of pure air, that

* Mr. Scheele alſo obſerved that ſome mercury in its metallic ſtate always remains in the nitrous ſolution of mercury. P. 222 of the French edition of his works.

is,

is, it was what we called dephlogiſticated nitrous acid; 100 gr. of ſuch acid we have already ſeen to contain 38 gr. of fixed air, and 62 of nitrous baſis, therefore the 200 gr. here decompoſed, contained 76 gr. of fixed air, and 124 of nitrous baſis; of theſe 124 gr. of nitrous baſis, 82,91 united immediately to part of the phlogiſton of the metal, namely, to 18,18 gr. of it, and formed with it 101,09 gr. of nitrous air, which were caught in the receiver. The remainder of the nitrous baſis, that is, 41,09 gr. remained in the ſolution, and were decompoſed towards the middle of the operation. To underſtand this decompoſition, it is neceſſary to recollect that metallic ſubſtances, in uniting to nitrous acid, unite to it principally through their affinity to the acidifying principle, namely, to fixed air, and take up the baſis chiefly by reaſon of the union of this baſis to the acidifying principle. During the middle period of this experiment, the metal being heated gives out more phlogiſton than can be taken up by the undecompoſed nitrous baſis. This ſurplus is taken up by the pure air contained in the nitrous baſis, which pure air is thereby converted into fixed air, and unites to the metallic calx; the phlogiſticated air is therefore ſet looſe.

As the nitrous baſis conſiſts of pure air, and phlogiſticated air in the proportion of 2 to 1, the 41,09 gr. of nitrous baſis which remained in the ſolution, contained 27,42 of pure air,

and

and 13,67 gr. of phlogiſticated air; the pure air was converted into fixed air, by the phlogiſton of the metal, and the phlogiſticated air mixed partly with the nitrous air that eſcaped, and partly with the fixed air that remained with the metal; and when this was decompoſed during the revivification of the metal, a ſmall part of the phlogiſticated air was alſo decompoſed: in this manner, all the phænomena are exactly accounted for.

Thus we have, 1ſt. — —		161,09 gr. of nit. air.
2d. Pure air contained in 76 gr. of fixed air	63,08	
Pure air in the nitrous baſis	27,42	
	90,50	
3d. Mixture of phlogiſ. air, and pure air, from the decompoſition of part of it	7,33	97,83 dephlogiſ. air.
	97,83	
Total weight of air		198,92 grains.

Further, the mercury loſt 18,18 gr. of phlogiſton, carried off in the nitrous air; but this quantity was reſtored to it by the decompoſition of the 76 gr. of fixed air, originally contained in the nitrous acid, which contained 12,92 gr. of phlogiſton, and by the abſorption of that quantity of phlogiſton, which 200 gr. of this ſort of acid holds, which we have ſeen to amount to 11,44 gr. ſo that there is an exceſs of 6,2 gr. which compenſate for the phlogiſtication of the 19 gr. of undecompoſed acid, which were phlogiſticated at the

expence

expence of the metal, and paſſed over into the receiver as already mentioned.

But it may be ſaid, that according to my table of the abſolute weight of phlogiſton in metals, 100 gr. of mercury contain 4,56 gr. of phlogiſton, and, conſequently, 900 gr. ſhould contain 41,04, and therefore much more ſhould be reſtored to it, than was here ſet forth. To which I anſwer, that part of it was employed in the converſion of 27,42 gr. of pure air in the decompoſed nitrous baſis, into fixed air, and part united to the compound of acid and calx, which, as Scheele remarked, takes up more phlogiſton than either ſingly, and in the end the whole was reſorbed by the metal.

Here it will be proper to obſerve, that the ſame decompoſition of the nitrous baſis, which happens during the ſolution of mercury with heat, takes place in a much greater degree during the ſolution of zinc, tin, iron, and regulus of antimony.

Mr. Watt, and a few others, ſuſpect that the dephlogiſticated air, in this and all other caſes where the nitrous acid ſeems to be decompoſed, ariſes entirely from the dephlogiſtication of water, whoſe phlogiſton, they ſay, is taken up by the nitrous acid, or by the metal: but ſurely the mixture of phlogiſticated air, which is always found with the dephlogiſticated air, cannot be derived from the water. Beſides, the ſame quantity of acid and water cannot be recovered by the union of both

airs, as it ſhould were this theory exact, for ſome dephlogiſticated air always remains, that cannot be combined; and that the acid is decompoſed is evident, for the half of it cannot be recovered.

Independently of metallic ſubſtances which give a tinge to nitrous acid, its colour depends, as has been already ſaid, on the proportion of nitrous air combined with it. Hence, if a bottle ½ full of colourleſs nitrous acid, be expoſed to the light, it becomes of a greeniſh yellow, and dephlogiſticated air is produced; for *light* has the property of increaſing the capacity of the dephlogiſticated part of fixed air for containing fire, and, conſequently, of diminiſhing its union with phlogiſton; the phlogiſton then unites to a part of the nitrous baſis, and becomes nitrous air, which combines with the nitrous acid, and tinges it. When the bottle is full, the dephlogiſticated air cannot be ſeparated, and, conſequently, no decompoſition can take place.

If nitrous air be mixed with its own weight of hepatic air, the hepatic air attracts the nitrous vapour generally diffuſed through the nitrous air, and this vapour drags with it the phlogiſton of the nitrous air. By theſe attractions the capacities are changed, and the quantity of fire neceſſary to the fluid ſtate eſcapes; conſequently, both the ſulphur, the nitrous vapour, and much of the phlogiſton are precipitated. Hence the water with which this

this precipitate is waſhed, precipitates the nitrous ſolution of ſilver white*, which Mr. Cavendiſh diſcovered to be a character of the phlogiſticated nitrous acid. The nitrous baſis is then left almoſt perfectly pure and dephlogiſticated; and as it contains double the portion of dephlogiſticated air that it does of phlogiſticated, it admits a candle to burn naturally, or even better than in common air, according as it is more or leſs perfectly deacidified and dephlogiſticated; the deacidification, and conſequent dephlogiſtication, is brought about in the ſame manner, by expoſure to iron or liver of ſulphur.

* This is mentioned in my Diſſertation on Hepatic Air.

OBSERVATIONS

ON THE

NITRIC ACID,

BY

Mr. BERTHOLLET.

THE ideas which Mr. Kirwan preſents on the compoſition of the nitric acid, are all founded ultimately upon the ſuppoſition that phlogiſticated air, or azotic gas, contains phlogiſton; and he pretends to prove this by the ſtate in which the acid is found, which is formed in the experiment of Mr. Cavendiſh; for this acid, which, acording to his manner of viewing the ſubject, is phlogiſticated, owes this ſtate to the nitrous gas, which it holds in ſolution, ſee page 82. Now the nitrous gas contains phlogiſton, becauſe the nitric acid dephlogiſticates ſulphur, and is by that means changed partly into nitrous gas. But if we come to the proofs of the exiſtence of phlogiſton in ſulphur, we find that ſulphur contains phlogiſton, becauſe when treated with the nitric acid, it forms nitrous gas, page 68, ſo that all this courſe of reaſoning, all the explanations which we read in

in the preſent ſection, and all the calculations of the quantities of phlogiſton which exiſt in the different ſtates of the nitric acid, are grounded principally upon this vicious circle; nitrous gas contains phlogiſton, becauſe it has taken it from ſulphur; ſulphur contains phlogiſton, becauſe it has converted the nitric acid into nitrous gas.

The following facts are agreed on. 1. When nitre is decompoſed by the action of heat, vital air and azotic gas, or phlogiſticated air, are obtained, both of which have reſumed the gaſeous ſtate by combining with a ſufficient quantity of caloric and the principle of light. It is clear that the ſmall portion which eſcapes decompoſition, whether in the form of nitrous acid, or of nitrous vapour, might have likewiſe been decompoſed; ſo that we may conſider the decompoſition as total.

2. Mr. Cavendiſh reproduced nitrous acid by ſubjecting a mixture of azotic gas and vital air to the action of the electric ſpark; and he has lately repeated this fine experiment in an authentic manner. The nitric acid affords therefore, by decompoſition, the ſame principles which are capable of reproducing it.

But it has been obſerved, that a very ſmall quantity of carbonic acid is diſengaged at the commencement of the decompoſition of nitre by heat. Hence Mr. Kirwan concludes, that the carbonic acid, or fixed air, is a conſtituent part of the nitric acid; nevertheleſs, it appears to

me to be inconteſtible, that this ſmall quantity of carbonic acid is merely a production ariſing from ſome principle foreign to the nitric acid; for if when this portion of carbonic acid is diſengaged, the proceſs be ſtopped, and the nitre diſſolved in water, it is recovered again by cryſtalization, for the moſt part in its natural ſtate. All the nitre which is decompoſed after this period, affords no carbonic acid; the preſence of this acid is therefore nothing but an accident, and we ſhall hereafter explain why this accident ſo eaſily takes place.

By following the different decompoſitions, we find, in them all, the two principles we have acknowledged, and nothing elſe. If any ſubſtance poſſeſs the property of depriving nitric acid of part of its oxigene, it reduces it to nitrous gas, in which we may find, either by the action of ſome metals, or of the ſulfures of alkalies, [hepars] the two ſame principles, but in different proportions, becauſe a portion of the oxigene, which conſtituted the nitric acid, has been taken from it. Laſtly, if we preſent to the nitric acid a ſubſtance which can ſeize the whole of its oxigene, there is then no other ſubſtance diſengaged but azotic gas. There is a gas which greatly reſembles nitrous gas, and which Mr. Prieſtley calls dephlogiſticated nitrous gas: its conſtitution is not yet well eſtabliſhed; the proportions of its principles are unknown, and its relations

with

with nitrous gas and the nitric acid have not been determined with ſufficient preciſion; ſo that no induction can hence be drawn, either in favour of or againſt the exiſtence of phlogiſton. If we were diſpoſed to content ourſelves with vague explanations, it would be eaſy to oppoſe one to that of Mr. Kirwan.

The facts which Mr. Kirwan here oppoſes, may be clearly explained without adding any ſuppoſition to the immediate reſults of experiment. We ſhall proceed to conſider the chief of them.

I have obtained the carbonic acid, principally by treating ſteel and zinc with nitre; I did not at that time know that theſe two metals contained charcoal; but this is a thing ſo well proved at preſent, that no further doubt ought to remain concerning the origin of this acid, and that it ought not even to be a matter of ſurprize that it is obtained from them in a quantity ſomewhat conſiderable.

1. Becauſe a given weight of carbure of iron, or plumbago, ought to form with oxigene, more than three times its weight of carbonic acid; inſtead of which, Mr. Kirwan ſuppoſes, with Scheele, that it ought not to afford more than the third part of its weight, ſo that the difference is nearly as ten to one.
2. Becauſe the quantity of carbure of iron, which is obtained from ſolutions of that metal, is always leſs than really exiſted in it,

as has been ſhewn in the memoir upon the different ſtates of iron. 3. Becauſe no more than a very ſmall quantity of carbonic acid is required to render lime water turbid, as the experiments related by Mr. Kirwan himſelf in another place prove. This learned chymiſt aſſerts, in his remarks on the experiments of Mr. Cavendiſh on air, that if a cubic inch of carbonic acid be diſſolved in 3 ounces of water, a few drops only of the water will be ſufficient to render lime water turbid; and he concludes, from ſeveral obſervations, that one thouſandth part of a cubic inch of carbonic acid may be rendered perceptible: Now as one part of charcoal produces near 3 parts of carbonic acid, by its combination with oxigene, it muſt follow that no greater quantity of charcoal, than about the weight of one four thouſandth part of a cubic inch of carbonic acid, is neceſſary to form a quantity of this acid, which ſhall be perceptible by the teſt of lime water.

Theſe conſiderations explain why it is ſo difficult to treat by fire, any ſubſtance which contains oxigene, without obtaining a ſmall portion of carbonic acid; for if it has been expoſed to the open air, it is ſufficient that a particle ſhall have attached itſelf to it, which contains one ſix thouſandth of a grain of charcoal, becauſe the weight of a cubic inch of carbonic acid may be valued at two thirds of a grain. Moreover, the carbonic acid,

acid, which is held in ſolution by the air of the atmoſphere, is fixable by a great variety of ſubſtances; ſo that when the red oxide of mercury is expoſed to diſtillation, a greater or leſs quantity of carbonic acid is always obtained, unleſs thoſe precautions be taken which were uſed by Mr. Monge in procuring the large quantity of vital air, which was required for his experiments on the compoſition of water; he diſſolved the mercury in nitrous acid, in retorts from which he afterwards expelled the acid and the nitrous gas, and obtained the vital air by continuing the operation: all this vital air did not afford the ſmalleſt indication of carbonic acid. We ſee therefore that the carbonic acid which is obtained in the diſtillation of the mercurial oxide, owes its origin neither to the nitrous acid nor the mercury, and that it is not by means of the ſmall quantities of carbonic acid, which muſt be obtained in moſt chemical operations, that the direct and rigourous proofs which Mr. Lavoiſier has given of its compoſition can be weakened.

At the time when I made my experiments upon the decompoſition of nitre, I was not aware of the difference which might be produced in the reſults by uſing ſteel or iron, and I poſitively aſſerted, in the Memoirs of 1781, that I had made uſe of ſteel; Mr. Kirwan, on the contrary, ſuppoſes that I uſed ductile iron; laſtly, ſince that time having learned that

that Scheele had detonated antimony and nitre without obtaining carbonic acid, I have treated that metallic ſubſtance with nitre in different proportions, and with the neceſſary precautions, which produced the ſame reſult as that of Scheele, though the detonation was very ſtrong. The production of carbonic acid is not therefore an effect which neceſſarily depends on the detonation of metallic ſubſtances, when it is accompained with much heat; and it is not the degree of heat which determines the formation of water, or of carbonic acid, as is likewiſe proved from many other facts.

The diminution of nitrous gas by the electric ſpark, which Mr. Kirwan attributes to a formation of water, is owing to the combination of the mercury with the oxigene, which exiſted in the gas, as I have remarked in the Memoirs of the Academy for 1785. In order to explain the obſervations of Meſſrs. Prieſtley and Van Marum, Mr. Kirwan is obliged to ſuppoſe that the nitrous gas contained nitrous vapour, as he ſays it almoſt always does; but nitrous gas, which is colourleſs, and has been paſſed through water, does not contain nitrous vapours.

When Mr. Lichtenſtein diſtilled a mixture of nitric acid and charcoal, he did not examine the vapours which were diſengaged, as may be eaſily ſeen from the deſcription of his experiments, and the conſequences he draws from them; but Mr. Lavoiſier and Mr. Haſſenfratz

ſenfratz have both aſcertained that a great quantity of nitrous gas is diſengaged, which is mixed with carbonic acid.

Mr Kirwan inſiſts upon two experiments to prove the decompoſition of carbonic acid. The firſt is taken from Dr. Prieſtley, who affirms that he obtained vital air, by diſtillation, from the acetic acid or radical vinegar with lime: Mr. Kirwan calls this combination ſimply, acetous ſelenite, without diſtinguiſhing the acetous acid, from that which has hitherto been called radical vinegar, and was uſed by Dr. Prieſtley; ſee his 4th vol. page 309. It is nevertheleſs upon this diſtinction that the ſolution of the fact depends, as has likewiſe been obſerved by Mr. De Fourcroy. The radical vinegar, or acetic acid, differs from the acetous acid in having received a greater quantity of oxigene into its combination; and it is this part of its oxigene which is diſengaged by means of lime.

The ſecond experiment urged by Mr. Kirwan, is likewiſe taken from Dr. Prieſtley; Experiments and Obſervations, vol. 4th, page 242. He ſubmitted a calcareous ſtone to diſtillation, and the air which paſſed towards the end of the proceſs, was nearly of the ſame purity as the air of the atmoſphere. But I would aſk Mr. Kirwan, why he has rather choſen to avail himſelf of this experiment, than of that which immediately follows it, and in which the author affirms that the re-

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ſidue of a like diſtillation was phlogiſticated air, and that the laſt portion contained as much phlogiſticated as fixed air? Might not Mr. Kirwan equally prove that manganeſe contains phlogiſton, becauſe, in the ſame ſeries of experiments, Dr. Prieſtley obtained from a ſpecimen of manganeſe 1200 meaſures of air, $\frac{2}{3}$ of which were inflammable, and burned with a blue flame; page 246? It is not by a few inſulated experiments, made without any determinate intention, that an oppoſition can be made to truths eſtabliſhed by a ſeries of facts, which mutually explain each other. The celebrated Prieſtley has himſelf often ſet us the example, by rectifying the reſults of ſome of his numerous experiments.

It is not here denied that the carbonic acid is never decompoſed, but there is no chemical fact yet known, in which it may be even conjectured that this decompoſition takes place.

I do not agree with Mr. Kirwan, when he ſays, that vital air is not diſengaged by expoſing a bottle containing nitric acid to the action of light, if it be perfectly full. It is neceſſary only that the vital air which tends to diſengage itſelf, ſhall be at liberty to eſcape, or ſuffer no other reſiſtance than ſuch as it is capable of overcoming. It is proper however to obſerve, that vital air is not diſengaged if the veſſel be very ſmall.

Before we poſſeſſed accurate notions of the principles which conſtitute the nitric acid,

Mr.

Mr. Lavoiſier had conſidered it as a compound of nitrous gas and oxigene; and had by that means explained its effects upon metals, and the acidity it communicates to ſulphur, phoſphorus, and ſome other ſubſtances: this was a great ſtep, and it was not then poſſible to approach nearer the truth. But in the calculations he made to determine the reſpective quantities of theſe two principles, by ſeparating them by means of mercury, and recombining them afterwards to form the nitric acid again, an error crept in, which it was not in his power to explain, becauſe part of the nitrous acid was reduced to its laſt principles, namely azotic gas and vital air, ſo that in the recompoſition a greater or leſs exceſs of vital air was found. But at preſent the cauſe of this is ſo clearly ſeen, that it appears uſeleſs to dwell upon it.

SECT.

SECT. V.

Of the Marine Acid.

COMMON marine acid appears to me to conſiſt of a peculiar baſis united to phlogiſton, and a certain proportion of fixed air, to both of which the baſis ſeems to have a ſtrong affinity.

If the marine baſis be deprived of its phlogiſton, its affinity to fixed air becomes much ſtronger; it unites to ſo large a portion of it, that the affinities of the reſulting acid, to bodies that contain little or no phlogiſton, become nearly as weak as thoſe of fixed air itſelf, equally condenſed: but with reſpect to bodies that contain a conſiderable proportion of phlogiſton, its affinities are much ſtronger, as its baſis attracts the phlogiſton, while thoſe bodies attract its exceſs of fixed air. The acid reſulting from the union of the dephlogiſticated baſis, with an exceſs of fixed air, is called the *dephlogiſticated marine acid.*

Before the diſcoveries of Mr. Berthollet, the properties of this acid ſeemed to me to furniſh ſtrong proofs of the falſehood of the antiphlogiſtic theory; but they appear in quite a different light ſince the publication of the experiments

ments of this excellent chymiſt, in ſo much that, I muſt own, they alone ſeem to me to afford any plauſible ground for that hypotheſis.

According to the antiphlogiſtians, then, the common marine acid conſiſts of a peculiar baſis united to a ſmall proportion of pure air, or oxigenous principle, and the dephlogiſticated marine acid differs from it, only by containing an exceſs of this principle.

If the common marine acid be diſtilled over the black calx of manganeſe, or minium, it becomes dephlogiſticated, as the immortal Scheele has firſt diſcovered; but then it unites to a conſiderable proportion of the air contained in thoſe calces, as appears by the experiments of Meſſrs. Berthollet and Pelletier*. According to Mr. Lavoiſier's table, the baſis of the marine acid has a ſtronger affinity to the oxigenous principle than any metallic calx, or the baſis of any acid, has to that principle; why then does it not become dephlogiſticated by diſtillation over the calces of iron or over the vitriolic acid? and why does it not convert this acid into ſulphur? is it not becauſe theſe ſubſtances cannot dephlogiſticate it?

The dephlogiſticated marine acid unites to water almoſt as difficultly as fixed air, becauſe being over ſaturated with that air, it participates in a great degree of its properties.

This acid does not expel fixed air from

* 26 Roz. 322, and 389.

aerated

aerated fixed alkalis or earths, until it is heated, and then dephlogiſticated air ſeparates from it, and it becomes in all reſpects common marine acid. For as it contains an exceſs of fixed air, it acts nearly as an acid of the ſame nature; but when heat is applied, its baſis dephlogiſticates its own fixed air, which then becomes dephlogiſticated air, at the ſame time that the acid becomes *common marine acid*, and acts as ſuch. Heat alone would not dephlogiſticate this acid, becauſe of its volatility; its affinity to alkalis detains it, and helps its decompoſition. But the dephlogiſticated marine acid unites and effervesces with volatile alkalis, whether aerated or cauſtic, becauſe theſe alkalis are compoſed of inflammable air, and phlogiſticated air; the marine baſis ſeizes the inflammable, and ſets looſe the phlogiſticated air.

It deſtroys vegetable colours, by depriving the colouring matter of its phlogiſton, and ſaturating it with fixed air. And hence the colour is not reſtored by the addition of an alkali, as the alkalis cannot reſtore the phlogiſton.

All metallic ſubſtances are ſoluble in the dephlogiſticated acid, without affording inflammable air; becauſe the phlogiſton ſeparated from them, is abſorbed by the marine baſis, and the compound of acid and calx.

If a ſolution of mercury in the nitrous acid be dropped into common marine acid, it forms a white precipitate, which is phlogiſticated,

ſince

ſince it affords red vapours, when re-diſſolved in the nitrous acid. But if the nitrous ſolution of mercury be dropped into dephlogiſticated marine acid, it forms ſublimate corroſive, which does not give red vapours when the nitrous acid is poured on it. The reaſon is, becauſe in the firſt caſe, the quantity of nitrous acid is too ſmall to dephlogiſticate the marine which expels it; but in the ſecond caſe, the marine is already dephlogiſticated. This is the teſt Mr. Berthollet uſes for diſtinguiſhing the dephlogiſticated marine acid.

The experiments which chiefly induce the antiphlogiſtians to maintain the preſence of pure air in the dephlogiſticated marine acid, are the following:

1ſt. Becauſe this acid is procured by diſtilling it from manganeſe, and the manganeſe, if diſtilled by itſelf, before the acid is diſtilled from it, affords dephlogiſticated air; but after the acid is diſtilled from it, it gives none.

But this experiment proves no more, but that the manganeſe contains ſome air which is dephlogiſticated during calcination, and that this air is fixed air, appears from the following conſiderations. The black calx of manganeſe almoſt always gives out fixed air at firſt, before any dephlogiſticated air appears, whence it is natural to think that the dephlogiſticated air proceeds from the dephlogiſtication of the fixed. And hence if it be diſtilled with filings of iron, or in a gun barrel, it ſcarce gives out

any other than fixed air*; if at any time it gives out dephlogiſticated air, with little or no mixture of fixed air, this is owing to a very perfect dephlogiſtication of the calx, and to its containing very little moiſture; thus Dr. Prieſtley having paſſed the ſteam of boiling water through manganeſe heated in an earthen tube, obtained a very large quantity of fixed air, and ſcarce any other†; though, on repeating this experiment with manganeſe well freed from calcareous earth, I obtained a large proportion of dephlogiſticated air; but I believe much depends on the degree of heat to which the tube is ſubjected. But having diſtilled manganeſe, which yielded of itſelf ſome fixed air, with common ſpirit of ſalt, I obtained dephlogiſticated marine acid, and not a particle of fixed air, which ſhews that this laſt combined with the dephlogiſticated baſis, and formed the dephlogiſticated acid. Mr. Hermſtadt, a German chymiſt of the higheſt reputation, having diſſolved the black calx in common marine acid, and precipitated it with an aerated fixed alkali, obtained, as uſual, a white precipitate, which, when heated, afforded a great part of the fixed air it had abſorbed from the alkali; but when heated to ſuch a degree as to be of a brown red colour, and conſequently dephlogiſticated, it converted common ſpirit of ſalt into a dephlogiſticated acid, which could pro-

* 4 Pr. 239. 1 Hermſt. Phyſ. Chym. Verſuche, p. 277.
† 6 Pr. 354. 1 Hermſt. 173.

ceed

ceed only from ſome fixed air, yet unexpelled. Yet if ſal ammoniac be diſtilled with the black calx of manganeſe, it will be expelled in a cauſtic ſtate; for the fixed air unites to the dephlogiſticated marine baſis in preference to the volatile alkali.

If equal quantities of inflammable air and dephlogiſticated marine air be mixed, a denſe white cloud immediately appears, $\frac{1}{2}$ of the bulk of both airs is ſoon abſorbed, and is found to be common marine acid. The reſiduum is ſaid to detonate like a mixture of inflammable and dephlogiſticated air*. As this experiment ſeemed to be of great importance, I repeated it; and having mixed 6 cubic inches of inflammable air with 6 of dephlogiſticated marine air over water, I obſerved a denſe white cloud immediately formed, attended with a diminution of 1 cubic inch; but in $\frac{1}{2}$ an hour 7 cubic inches were abſorbed: into the reſiduum, I put a bit of phoſphorus ſtuck on an iron wire, and endeavoured in vain to fire it by approaching a red hot iron on the outſide. It ſhone, and even ſmoked and ſublimed, but no detonation took place, ſo that clearly the reſiduum was not a mixture of inflammable and dephlogiſticated air: the detonation obſerved by Mr. Pelletier, muſt rather have proceeded from the union of the inflammable and dephlogiſticated marine air.

* 26 Roz. 453.

For greater certainty I again mixed equal quantities of both airs, and after more than ½ diſappeared, I fired the reſiduum in a narrow-mouthed bottle, and found it to give 4 ſucceſſive exploſions, which evidently proves it was mere inflammable air, and not a mixture of inflammable and dephlogiſticated air. This experiment eſtabliſhes, beyond all doubt, that inflammable air unites to dephlogiſticated marine air, and converts it into common marine acid. To try whether the dephlogiſticated marine air were united to fixed air, I mixed 6 cubic inches of inflammable air once more, with 6 of marine air, over lime-water; in about 10 minutes after the greater part of the diminution had taken place, a white cloud appeared on the ſurface of the lime-water, and by agitation it became ſtill more turbid: as it was poſſible that the manganeſe might be mixed with calcareous earth, I extracted from another portion of it, ſome dephlogiſticated marine air, and received it on lime-water, but it was wholly abſorbed, without forming the leaſt cloud, though there was lime enough; for on adding aerated water, a cloud appeared. This experiment therefore fully confirms my opinion, and ſubverts that of the antiphlogiſtians. Even if the manganeſe had contained calcareous earth, this would not affect my theory, for I have obtained dephlogiſticated marine acid from chalk, and Mr. Galliſh obtained it from magneſia; for the fixed

fixed air unites to the acid as ſoon as it parts with its phlogiſton.

If nitrous air be mixed with dephlogiſticated marine air over water, both immediately become viſible and are abſorbed*. Here a double decompoſition takes places, by virtue of which, the common marine acid, and the nitrous acid, are regenerated: the marine air dephlogiſticates the nitrous air, and at the ſame time gives to the nitrous baſis its acidifying principle.

If ſulphur be expoſed to the action of the concentrated dephlogiſticated marine acid, it is decompoſed, and the marine acid becomes common ſpirit of ſalt†. This ſhews that ſulphur contains the ſame principle as inflammable air, which, as we have juſt ſeen, reſtores the dephlogiſticated acid to its common ſtate. Phoſphorus alſo is decompoſed with the aſſiſtance of heat.

If dephlogiſticated marine acid be expoſed to the ſolar light, it emits dephlogiſticated air, and becomes common marine acid‡; the fixed air being decompoſed, as already ſeen, p. 114.

Mr. Berthollet and Morveau tried in vain to combine dephlogiſticated air directly with the common marine acid. 1 Encyclop. p. 254.

* 26 Roz. 393. par Pelletier. † 1 Nouvelle Encyclop. 252. Chy. Beytr. 1 Band. 3 Stuck.
‡ 29 Roz. 82.

OBSERVATIONS

ON THE

MURIATIC ACID,

BY

MR. BERTHOLLET.

ACCORDING to the ſuppoſition of Mr. Kirwan, the muriatic acid is compoſed of a peculiar baſe, united to phlogiſton, and to a certain quantity of fixed air, which laſt, according to him, is compoſed of phlogiſton and oxigene: when manganeſe dephlogiſticates the muriatic acid, it deprives it of its phlogiſton, and gives it fixed air. The muriatic acid, therefore, is compoſed of a baſe with phlogiſton and oxigene; and when it is dephlogiſticated, it is likewiſe compoſed of a baſe with phlogiſton and oxigene in other proportions.

But when the muriatic acid has been oxigenated, the action of light re-eſtabliſhes it in its firſt ſtate, by diſengaging the vital air which was fixed in it. Mr. Kirwan agrees that light does nothing more than reſtore the elaſticity of the oxigene; therefore the muriatic acid muſt

muſt have preſerved all the phlogiſton which belonged to it, and the manganeſe did not deprive it of any. If it be ſaid that the light has reſtored its phlogiſton, it will be neceſſary to ſuppoſe that the light has reſtored hydrogenous gas; an opinion which cannot be maintained.

When Mr. Kirwan admits that the action of light re-eſtabliſhes the oxigenated muriatic acid in its original ſtate, by reſtoring the elaſticity of its oxigene, ought he not to admit, that this oxigene is the only real difference between the oxigenated muriatic acid and the common muriatic acid? Is not the phlogiſton therefore which he ſuppoſes, an uſeleſs being, which has no influence in any of the phenomena we have endeavoured to explain, relating to the properties of the oxigenated muriatic acid? If hydrogene exiſts in the muriatic acid, there is no fact which ſhews its exiſtence; its exiſtence, therefore, can only be gueſſed at.

Mr. Kirwan acknowledges that hydrogenous gas does not detonate when mixed with the oxigenated muriatic gas; but he pretends that carbonic acid is formed, and conſequently that the oxigenated muriatic acid reſumes its original ſtate. I paſſed, ſeveral ſucceſſive times, the oxigenated muriatic gas into hydrogenous gas, and each time I agitated the mixture over water. The oxigenated muriatic acid was abſorbed, without having experienced any change; it was not reſtored to the ſtate of

common muriatic acid, as Mr. Kirwan pretends, neither was the hydrogenous gas in any way altered or diminiſhed. Memoirs of the Academy, 1785.

The carbonic acid, which is diſengaged from manganeſe, ſerves, according to Mr. Kirwan, to form the oxigenated muriatic acid; it is chiefly from the calcareous parts, which are almoſt always mixed with the oxide of manganeſe, that the carbonic acid is extricated. But it is ſo far from contributing to the production of oxigenated muriatic acid, that manganeſe, which has been deprived of it by means of the ſulphuric acid, is much more proper to be uſed in preparing the oxigenated muriatic acid, eſpecially when the operation is to be made in the large way, becauſe, by this means, the efferveſcence which takes place at the commencement is avoided; for it ariſes merely from the diſengagement of the carbonic acid.

When Mr. Lavoiſier attributed to the baſe of the muriatic acid, a ſtronger affinity with the oxigene than with metals, he did not pretend to ſpeak of that portion of oxigene, which, from ſtrong analogies, he ſuppoſes to exiſt in the common muriatic acid, and cannot be diſengaged by any known means; Mr. Kirwan, in his objections, confounds this with the oxigene, which, by combining in exceſs with the muriatic acid, changes it into oxigenated muriatic acid, and which quits it with great facility.

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The obſervation of Mr. Hermſtadt is not at all contrary to our doctrine. With regard to the oxigenated muriatic acid, which in one experiment was produced by means of chalk, it is natural to attribute it to ſome foreign ſubſtance, probably the nitric acid which might have exiſted in the chalk, or in the muriatic acid made uſe of.

SECT.

SECT VI.

Of Aqua Regia.

IF the common marine acid be mixed with an equal bulk of ſtrong colourleſs nitrous acid, the marine will deacidify in great meaſure the nitrous, while the nitrous dephlogiſticates the marine; that is to ſay, the marine will take up a great part of the fixed air of the nitrous acid, while the nitrous will take up the phlogiſton of the marine. Hence part of the nitrous acid is converted into nitrous air, which immediately unites to the undecompoſed part of the nitrous acid, and forms phlogiſticated nitrous acid, and hence the red colour of the liquor.

If the nitrous acid be in ſmall proportion, it will be wholly decompoſed; for the marine baſis, and the phlogiſton of that part which is converted into nitrous air, both ſolicit the pure air in the nitrous baſis, which, when diſengaged, is converted into fixed air, and unites to the marine baſis, and the phlogiſticated air is ſet looſe*.

* See the curious Experiments of Mr. Pelletier, 26 Roz. 393.

Thence

Thence if the marine acid be made to imbibe nitrous vapour, a very ſtrong aqua regia will be produced, as Dr. Prieſtley has diſcovered; for nitrous vapour contains a large proportion of nitrous baſis, as already ſhewn, and very little water, and this baſis being decompoſed affords a larger quantity of fixed air to the marine baſis, than triple the bulk of aqueous nitrous acid.

Shortly after the mixture of the nitrous and marine acids, an air ariſes which is immediately abſorbed by water, 26 Roz. 323; becauſe it is a mixture of dephlogiſticated marine air and of nitrous air, and theſe decompoſe each other, and form nitrous and common marine acids.

When aqua regia is made with a certain proportion of ſal ammoniac, the volatile alkali is deſtroyed; for when the marine acid is dephlogiſticated, it reacts upon and decompoſes the volatile alkali.

But as water in the common temperature of the atmoſphere, can retain but a very inconſiderable quantity of dephlogiſticated marine acid, it ſeems very difficult to explain why in aqua regia ſo conſiderable a quantity of that acid remains. This appears to me to be occaſioned by its affinity to the undecompoſed nitrous acid; to ſee if that were the caſe, I mixed the nitrous and marine acids in different proportions, and examined whether the ſpecific gravity of the mixture were greater

than

than the mean that ſhould reſult, and I always found it leſs; but as during the union of the two acids, and while weighing, a great quantity of air eſcapes, no concluſion can be drawn from theſe experiments.

The antiphlogiſtic explanation of theſe phænomena appears to me perplexed and difficult to underſtand. According to Mr. Berthollet*, though nitrous air attracts the oxigenous principle more ſtrongly than marine acid attracts it, "yet by a double affinity on the "one hand the nitrous air combines with the "marine acid, and nitrous acid of the aqua "regia, and on the other, the vital air of "part of the nitrous acid combines with part "of the marine acid." With reſpect to the affinity of nitrous air to marine acid, it can ſcarce be allowed; for, according to the experiments of Dr. Prieſtley, the marine acid ſcarcely abſorbs any in a *ſhort* time, and not above $\frac{1}{4}$ of its bulk even in 2 months†, whereas aqua regia is made in $\frac{1}{2}$ an hour; and upon the whole, this explanation ſays no more than that the two acids unite, ſince the marine acid unites to both principles of the nitrous acid, viz. the nitrous air and vital air; yet that ſomething more happens is evident even by the ſmell, for this is the ſame as that of marine acid digeſted with manganeſe.

* 1 Encyclop. 259. † 3 Pr. 129.

OBSER-

OBSERVATIONS

ON

AQUA REGIA,

OR THE

NITRO MURIATIC ACID.

BY

Mr. BERTHOLLET.

WE have ſeen in the preceding ſection, that the oxigenated muriatic acid could not have loſt phlogiſton, becauſe if the oxigene be ſeparated merely by the aſſiſtance of light, it is reſtored to its primitive ſtate: the exchanges of phlogiſton, which Mr. Kirwan here ſuppoſes to take place between the muriatic and nitric acids, do not therefore require any new diſcuſſion.

Mr. Kirwan attributes to me an opinion which I find as unintelligble as he does, but which is very different from mine: he pretends that I conſider the nitrous gas as united to one part of the muriatic acid, while another part of this laſt is combined with the oxigene of the nitric acid, and that in the ſame

ſame liquor. But the part of the muriatic acid, which combines with the oxigene, does not remain in the liquid, but is diſengaged, and may be received in proportion as it is formed, at the expence of part of the oxigene of the nitric acid: the nitrous gas which reſults from the decompoſition of the nitric acid, remains in ſolution with the muriatic acid which is not oxigenated, and with that part of the nitric acid which has not been decompoſed. This is proved by the experiments I have deſcribed in the Memoirs of the Academy of Sciences for 1785.

It is with great reaſon that Mr. Kirwan finds it ſurpriſing, that the muriatic acid of the aqua regia can remain united in the oxigenated ſtate with a ſmall quantity of nitrous acid. It is indeed ſufficient to have compared aqua regia with the oxigenated muriatic acid in the ſtate of concentration we can obtain it in; it is enough to have taken notice of its extremely penetrating ſmell, and its great diſpoſition to fly off in vapours, though it neceſſarily contains a great quantity of water. Theſe obſervations are ſufficient to convince any one, that aqua regia does not conſiſt of this ſubſtance. A ſpeedy conviction may be obtained from obſerving the effects of aqua regia upon vegetable colours and alkalies; for theſe effects are ſimilar to thoſe which other acids produce, and conſequently very different from thoſe of the oxigenated muriatic acid. The

author

author therefore has made a mere ſuppoſition, when he affirmed that the volatile alkali is deſtroyed in the preparation of aqua regia by the amoniacal muriate; which is ſo far from being well founded, that the volatile alkali is no more decompoſed by the oxigenated muriatic acid at the temperature of the atmoſphere, than when it is itſelf combined with the muriatic or nitric acid.

SECT.

SECT. VII.

Of the Phoſphoric Acid.

FROM various experiments, and particularly thoſe of Mr. Lavoiſier, which appear to have been made with great accuracy, it appears that the phoſphoric acid conſiſts of a peculiar baſis united to 2,265 of its weight of the acidifying principle, that is, fixed air; or in other words, 100 gr. of dry phoſphoric acid contain about 69 of fixed air, and 31 of its peculiar baſis: 100 gr. of the phoſphoric baſis take up 226,5 of fixed air, or 32,9 of phlogiſton, when it becomes phoſphorus; and 100 gr. of phoſphorus contain 75,24 of baſis and 24,76 of phlogiſton.

The antiphlogiſtians think that the phoſphoric acid conſiſts of phoſphorus itſelf united to the oxigenous principle, and that phoſphorus does not contain phlogiſton.

Mr. Morveau made an experiment that evidently proves the dephlogiſtication of this ſubſtance during its acidification, and that pure air becomes fixed air before it unites to it: Having left a piece of phoſphorus in a large glaſs veſſel well ſtopped for 3 or 4 days, ex-

poſed to a temperature of 70 or 72°, and afterwards opened it in lime-water, the lime-water entered and became turbid, and being filtered, left a precipitate which effervesced with the nitrous acid, and conſequently the precipitation did not ariſe from the union of the lime with the phoſphoric acid. 1 Encyclop. p. 220.

Mr. Lavoiſier having *gradually* introduced a quantity of phoſphorus into nitrous acid, whoſe ſpecific gravity was 1,299 heated to *133°, obſerved a large quantity of nitrous air to be produced, and the phoſphorus almoſt wholly converted into phoſphoric acid, and increaſed in weight above the double†. As I have already ſhewn that nitrous air contains a large quantity of phlogiſton, and that it does not pre-exiſt in nitrous acid, I muſt conſider that produced on this occaſion, as a proof that phoſphorus contains phlogiſton, and that it took fixed air from the nitrous acid; but the ſurplus weight which the phoſphoric ſubſtance poſſeſſed after the operation, cannot be entirely derived from the nitrous acid, as much common air muſt have been admitted during the gradual introduction of the phoſphorus.

The celebrated Mr. Sage has ſhewn that phoſphorus precipitates copper, ſilver, and other metals from their diluted ſolutions in

* 39,1 of Reaumur. † Mem. Par. 1780, p. 350.

their metallic form, and that at the ſame time it is converted into an acid*. This is a full proof that phoſphorus contains phlogiſton, if metals contain any, when in their metallic form. If the phoſphoric acid be diſtilled with zinc, it will be converted into phoſphorus, 1 Margr. 146; ſo it will if diſtilled with tin, which contradicts Mr. Lavoiſier's table of affinities.

The baſis of the phoſphoric acid, as Mr. Morveau well remarks, is the only one which can be procured free, both from phlogiſton and the acidifying principle: it is what is called (though improperly, ſince it is not ſoluble in water) the glacial phoſphoric acid.

* 18 Roz. 263.

A LET-

A

LETTER

FROM

Mr. DE MORVEAU to Mr. HASSENFRATZ,

UPON THE

PHOSPHORIC ACID.

SIR,

YOU certainly could not have been embarraſſed for a reply to the argument which Mr. Kirwan builds upon my experiment in his ſection on the phoſphoric acid; but it is neceſſary, at the ſame time, to contradict the experiment itſelf, and you have the politeneſs to afford me an opportunity of rectifying this matter myſelf.

I ſay that you could not have been embarraſſed; for, in fact, the ſolution follows even from Mr. Kirwan's own hypotheſis. If fixed air be the acidifying principle, it is impoſſible that it ſhould have ſerved at the ſame time to acidify the phoſphorus, and render the lime effervescent. Was there a ſuperabundant portion? If ſo, why does not

it appear in the other operations when phoſphorus is acidified? How, upon this ſuppoſition, can the weight acquired by the phoſphorus be found to correſpond with that of the vital air abſorbed, &c. &c.

I might therefore, Sir, have confined myſelf to a reference to your own reflections, which would have been ſufficient to have overthrown the objection; but I have deferred my anſwer, until I could repeat the experiment with all the precautions neceſſary to render the reſult certain.

I placed 20 grains of phoſphorus, the pureſt I could get, and beautifully tranſparent, in a ſmall glaſs funnel blown at the lamp; I ſuſpended this funnel in a very large bottle, nearly at two thirds of its height; the ſtopper of the bottle carried a ſyphon, the extremity of which was plunged into a large veſſel filled with lime water, prepared the inſtant before. This bottle contained common air, which I had paſſed through lime water before I introduced it, in order that I might ſee whether it did by chance contain a ſmall quantity of diſengaged carbonic acid gas.

In a ſimilar bottle I cauſed vital air to enter, after having likewiſe paſſed it through lime water; and phoſphorus having been ſuſpended in the ſame manner in a funnel, a ſiphon of glaſs was inſerted, as in the former experiment, from the bottle, to a conſiderable depth under lime water.

In

In the experiment deſcribed page 220 of the Encyclopedie, I had only a bottle filled with common air; which determined me to operate this time as well on common as on vital air, as it might happen that the former might habitually contain a ſmall portion of carbonic gas in a ſtate of combination, which might prevent its affecting re-agents; and in this caſe it would not have been ſurpriſing that this portion ſhould have been ſeparated from the atmoſpheric fluid, at the ſame time that the phoſphorus deprived it of one of its conſtituent parts; but this effect did not take place.

In proportion as the phoſphorus burned away, (which did not require a long time, as I had expoſed the bottle to the rays of the ſun) the lime water entered to replace the abſorbed air. At the beginning, the acid which was formed fell through the neck of the funnel like a liquor, though it had ſtill manifeſtly a vaporous conſiſtence, which it preſerved on its arrival at the bottom of the veſſel. When the lime water had entered in a certain quantity, a white matter in flocks was depoſited.

By means of theſe apparatus the combuſtion of the phoſphorus was more ſpeedy, and likewiſe more complete. It continued in the firſt bottle until the whole portion of vital air was conſumed; it ſtopped in the ſecond, when

the lime water had riſen ſo as to cover the phoſphorus which remained.

I then opened the two bottles, and dipped blue paper into the fluid, which immediately became red. It therefore contained a ſuperabundant portion of phoſphoric acid; and hence it is evident, that the precipitate did not contain carbonic acid, becauſe the phoſphoric acid would have diſengaged it: on the contrary, it is very certain that a portion of the phoſphate of lime was held in ſolution by the exceſs of phoſphoric acid.

The carbonic acid gas did not exiſt above the fluid in the bottles; for if it had, it would have been attracted by the lime water in the ſiphon, whoſe diameter was upwards of three lines; it would have covered its ſides with carbonate of lime, or have left ſome traces at its orifice; or, at all events, it would have rendered the included fluid ſlightly turbid. But nothing of this happened; the lime water in the ſiphon preſerved all its tranſparency, while that of the veſſel which was in contact with the external air, was already covered with a pellicle of ſome thickneſs.

How then did it happen that I ſaw a movement of efferveſcence, when I poured the nitric acid the firſt time on a ſimilar precipitate? It is very certain that I did ſee it, becauſe I have deſcribed it; but I was led into an error by ſome foreign circumſtance. Who is there that does not know that, with

the

the beſt intentions, we are always diſpoſed to content ourſelves with appearances, when they agree with our explanations; and this is the reaſon why what we ſee always takes a tincture from what we think. It is not enough, however, to ſay that one has been deceived, it is neceſſary likewiſe to diſcover the cauſe of the error, in order to give confidence to a ſecond obſervation. It is this which engaged me to treat my precipitates in the ſame manner as in the experiment quoted by Mr. Kirwan. I have done more: before I threw them on the filter, I added lime water to exceſs in the two bottles; I cloſed them, and ſhook them ſtrongly; notwithſtanding this, the nitric acid rediſſolved them without diſengaging the ſmalleſt portion of gas. Indeed I ſubmitted to this proof the matter which remained on the filter when it was no longer immerſed in the fluid, and I did not think it neceſſary to let it dry as I had done, and mentioned in the account of the firſt experiment. This circumſtance is ſufficient to afford a reaſon for the difference in the phenomena obſerved, ſince, during the time of the deſiccation, the lime water with which the calcareous phoſphate was impregnated, might have received carbonic acid from the circumambient air.

I am, &c.

SECT VIII.

Of the Saccharine Acid.

VEGETABLE ſubſtances in general are reſolvable into water, fixed, inflammable, and phlogiſticated airs; in the number, proportion, and degree of condenſation of each of theſe, the ſole difference betwixt them lies; and if we ſuppoſe each of them to be capable of only 10 different degrees of condenſation, we ſhall have 40 principles, excluſive perhaps of fixed alkalis, whoſe compoſition is not yet known: the combinations of which theſe are capable, are fully ſufficient to furniſh all the varieties that can be ſuppoſed to exiſt. Every combination of two or more of theſe, and alſo every degree of condenſation, ſeems to have properties peculiar to it; but as we are in a great degree ignorant of the manner of combining or condenſing theſe principles, we are as yet unable to recompoſe even unorganized vegetable ſubſtances.

Sugar is a compound of fixed air with a much larger proportion of inflammable air and ſome water, all condenſed to a degree of which we are ignorant, but retaining upon the

the whole much more ſpecific heat than either oil or charcoal; this laſt indeed ſeems to exclude water from its compoſition. Mr. Morveau conjectures, with great probability, that ſugar has for its baſis a fine æthereal oil, to which a large proportion of condenſed inflammable air is ſuperadded.

The *acid of ſugar* conſiſts then of this peculiar baſis, ſtripped of its ſuperadded phlogiſton, and united to a large proportion of fixed air in a condenſed ſtate: the ſaccharine acid therefore does not pre-exiſt in ſugar, but is formed by the operation that exhibits it; and thus it differs from neutral ſalts, ſoaps, and phlogiſticated mineral acids.

This acid derives the greater part of its acidifiable principle from the nitrous acid, which, as well as the ſugar itſelf, is decompoſed during the operation that produces the acid of ſugar: the nitrous baſis takes up the phlogiſton of the ſugar, while the fixed air of the nitrous acid combines with the ſaccharine baſis.

In explaining many of the phænomena of the mineral acids, the antiphlogiſtic theory appears to great advantage from its ſeeming ſimplicity; but in explaining thoſe of the analyſis and production of the vegetable acids, this advantage is entirely loſt, and its inſufficiency becomes very apparent.

Mr. Lavoiſier diſtilled 236,25 gr. of ſugar, with 945 gr. of nitrous acid, whoſe ſpecific gravity

gravity was 1,316, diluted, with 945 gr. of water, in an apparatus for receiving airs, and an intermediate bottle for receiving the liquor that might paſs over during diſtillation. The total amount of the materials was therefore 2126,25 gr. and when the operation was over, the amount was*

		Grains.	
Nit. air 229,71 cubic inches	=	85	which contain 15 of
Fixed air 108,81	=	50,6	phlogiſton, and
Inflam. air 30,22	=	1	6,7 of nitrous
Liquor and ſalt in the retort	=	1316	baſis.
Weight gained by the intermediate bottle		599	
Total		2051,6	

Original Weight 2126,25 gr.
Deduct 2051,6

Loſs 74,65

This loſs is ſo conſiderable, that it were ſuperfluous to enter into an account of the

* Mr. Lavoiſier diſtilled 288 French grains of ſugar in 1157,9 of nitrous acid of the ſpecific gravity of 1,316, and diluted with 1157 grains of water. The total was therefore 2602 grains. He obtained

Nit. gas 189,74 c. inches, Fr.	=	103,7 gr.	which contain
Fixed air 89,877 -	=	61,732	18,2 of phlo-
Inflam. gas 24,99 -	=	1,22	giſton, and
Liquor and ſalt in the retort	=	1605,52	8,174 of ni-
Weight gained by the intermediate bottle		730,78	trous baſis.
Total		2502,952	

Original Weight 2602

Loſs 99,048

quantity

quantity of nitrous acid decompoſed*, and ſo much the more as the decompoſition of the nitrous acid is not conteſted. But he takes for granted what cannot be allowed, that the nitrous air pre-exiſted in the nitrous acid, and even that this acid contained an equal bulk of nitrous and pure air, which has been already ſhown to be impoſſible.

However, he infers from this experiment that ſugar is a *ſort* of charcoal, which uniting with the oxigenous principle of the nitrous acid, decompoſes that acid, ſets looſe the nitrous air, and forms the ſaccharine acid; but towards the end of the operation, the ſaccharine acid itſelf is, as he thinks, decompoſed, and hence the origin of the fixed air, which is nothing elſe but the oxigenous principle united to charcoal.

On this I remark, 1ſt. That according to this theory, the acid of ſugar and fixed air ſhould be one and the ſame thing, ſince both are compoſed of the oxigenous principle united to charcoal. Mr. Lavoiſier may reply, that the acid of ſugar, beſides charcoal, and the oxigenous principle, contains alſo inflammable air; but then he muſt own that

* Mem. Par. 1778, p. 541. There ſeems to be a contradiction in Mr. Lavoiſier's account, for he ſays, the intermediate bottle gained 1 oz. 2 gros and 12 gr. and a few lines after, that only 3 gros and 56 gr. had paſſed into it.

ſugar

ſugar contained a larger proportion of inflammable air, than was given out during the formation of the acid of ſugar, and cannot deny that part of this inflammable air united with the nitrous baſis, and formed nitrous air. He may perhaps alſo ſay, that this charcoal is different from common charcoal; but if ſo, how came it to make fixed air like common charcoal? Beſides, if it were a different ſort of charcoal, the acid of ſugar ſhould, in his ſyſtem, be decompoſed by common charcoal and ſugar regenerated; for, according to his table, charcoal has a much ſtronger affinity to the oxigenous principle than ſugar has to that principle. Nay, ſugar ſhould be regenerated by various metallic ſubſtances, which, by his table, ſtand before it in the order of attraction to the oxigenous principle.

2d. If the acid of ſugar conſiſted of ſugar itſelf united to the oxigenous principle, this acid ſhould weigh more than the ſugar itſelf of which it is formed, notwithſtanding that ſome fixed air and inflammable air eſcape from it. For in Mr. Lavoiſier's experiment, the quantity of ſugar employed was * 236,25 gr. the quantity of oxigenous principle taken up was † 83 gr. ſo that if there had been no loſs, the whole quantity of ſaccharine acid ſhould have been ‡ 319,25 gr. and if we deduct the

* 288, † 101,26. [‡ 349,485.

loſs

loſs of * 50 gr. of fixed air, and † 1 gr. of inflammable air, we ſtill have ‡ 268,25 gr. that is § 32 gr. more than the weight of the ſugar. But this increaſe of weight is contrary to the experience of all who have examined the matter with any accuracy. Mr. Bergman from 3 parts of ſugar obtained but 1 of ſaccharine acid ‖; Mr. Chaptal, from $\frac{1}{3}$ to $\frac{2}{3}$ of the quantity of ſugar employed ¶; Mr. Sage only $\frac{1}{10}$ *: and yet if we conſider the proportion and ſtrength of the acid employed by Mr. Lavoiſier, we ſhall find it very improbable that even the whole of the ſugar he employed was converted into ſaccharine acid.

3d. If the ſaccharine acid conſiſted of ſugar undecompoſed, and barely united to the oxigenous principle, then it ſhould be formed by treating ſugar with the black calx of manganeſe, or with dephlogiſticated marine acid; for both theſe ſubſtances contain abundance of the oxigenous principle, and eaſily give it out: yet after various trials, neither Mr. Scheele nor Mr. Morveau were able to form a particle of the ſaccharine acid, by means of either of theſe ſubſtances. Let it not be thought that this ariſes from want of affinity in the oxigenous principle to ſugar, for by Mr. Lavoiſier's table, it has a ſtronger affinity to ſugar than to either of theſe ſubſtances, and

* 61. † 1,22. ‡ 326,265. § 39,04. ‖ 1 Bergman, 253. ¶ Chaptal, 61. * Mem. Par. 1777, p. 437.

paſſes

paſſes from them to ſulphur (to which, by that table, it has a weaker affinity), as Mr. Morveau has ſhewn. The only reaſon then, why ſugar cannot be converted into an acid by theſe ſubſtances, is, becauſe neither of them can ſtrip it, and carry off that quantity of phlogiſton which it muſt loſe before it can become an acid.

Laſtly, If the acid of ſugar be diſtilled, it is wholly converted into water, fixed and inflammable air, and not a particle either of coal or dephlogiſticated air is found in it. It is not therefore reaſonable to look on either of them as its conſtituent principles; but as fixed air alone can be extracted from all vegetable acids, it ſeems to be the true acidifiable principle.

REMARKS

REMARKS

ON THE

ACID OF SUGAR.

BY

MR. DE FOURCROY.

THOUGH we do not yet poſſeſs any very poſitive knowledge reſpecting the various principles which compoſe vegetable ſubſtances, the experiments of the moderns have nevertheleſs ſhewn, that theſe principles are much more ſimple, and leſs numerous, than was formerly thought; becauſe in the laſt analyſis nothing has been obtained from vegetables but the baſis of inflammable gas, which we call hydrogene; charcoal, which exiſts ready formed; oxigene, or the acidifying baſe of vital air; azote, or the baſe of azotic gas; and ſome earths. It is with theſe five or ſix primitive ſubſtances, which appear to be very ſimple, or whoſe component elements at leaſt have not yet been obtained ſeparate, that the work of vegetation produces extracts, inſipid mucilages, ſugar, fixed and volatile oils, aroma, gluten, farina, colouring matter, the various acids, &c.

All

All theſe vegetable matters do not appear to differ from each other, excepting in the number and proportion of their component parts, and, as Mr. Kirwan remarks, in the greater or leſs degree of condenſation to which thoſe parts are ſubjected.

It is the ſame with ſugar as with other vegetable matters: the moſt accurate analyſ exhibits no other primitive principles than hydrogene, carbone, water, and a ſmall quantity of earthy and alkaline matter; there is no fact which proves that it contains carbonic acid ready formed. Mr. Kirwan advances this aſſertion without poſitive proofs; every thing, on the contrary, announces that this acid, which is diſengaged by the action of fire, or by fermentation, is formed at the very inſtant of its diſengagement.

Mr. Kirwan thinks, with us, that the oxalic or ſaccharine acid does not pre-exiſt, but is produced by the action of the acid of nitre. But he differs in the explanation he gives; he thinks that the ethereal oil of the ſugar yields its hydrogene or phlogiſton to the nitrous baſis, which becomes nitrous gas, while the carbonic acid of this acid is fixed in the dephlogiſticated oil, and converts it into oxalic acid. Let us examine the juſt value of this theory. 1ſt. Mr. Kirwan has not demonſtrated the preſence of carbonic acid in the acid of nitre, nor even that the firſt of theſe acids is formed during the ſeparation of the principles,

and eſpecially of the vital air of the ſecond. But even if this aſſertion were demonſtrated, how can Mr. Kirwan explain why the inflammable gas or phlogiſton of the ſugar is diſengaged to unite with the nitrous baſis, and to reſume the ſame phlogiſton from this acid? If ſugar contain, according to him, all which is eſſential to become oxalic acid; ſince he admits the preſence of fixed air, why does it not change ſpontaneouſly into that acid? Why, in a word, does it quit its phlogiſton, to reſume it only in the ſtate of fixed air?

2d. If the converſion of the ethereal oil of ſugar, or the ſaccharine baſe into oxalic acid, conſiſts only in the diſengagement of its hydrogene or phlogiſton, and in the abſorption of the carbonic acid, why is not this acid formed by the diſtillation of ſugar, in which the two circumſtances neceſſary to this formation appear to be united?

3d. The preſence of the carbonic acid cannot be demonſtrated in the oxalic acid; the reciprocal converſion of the one into the other has not been effected in the ſame manner as the principles of thoſe acids, whoſe compoſition is rigorouſly demonſtrated in the modern doctrine of the French chemiſts, have been ſeparated and reunited.

The objections which Mr. Kirwan makes to this theory, relative to the formation of the oxalic acid, have not appeared to us as ſtrong as he thinks them. To anſwer with preciſion,

we ſhall in the firſt place remark, that the Memoir of Mr. Lavoiſier upon this acid, which is printed in the volume for 1778, from which Mr. Kirwan draws moſt of his arguments, is very far from what modern diſcoveries have more exactly taught us concerning the nature of vegetable ſubſtances. If reference were to be made only to ſuch works as have been written ten years ago, to aſcertain our theory, there would be a riſk of attributing to us inaccuracies, and even errors, which the experiments that have ſucceeded each other without interruption, ſince that epoch, have gradually removed. Mr. Lavoiſier has made more accurate reſearches concerning ſugar; and he would not now ſay that ſugar enters totally into the compoſition of the oxalic acid, or that its baſe conſiſts of charcoal. It reſults from his new reſearches upon ſugar, analized by the ſpiritous fermentation, that this vegetable ſubſtance contains, per quintal, near 8 pounds of hydrogene, 60 pounds of oxigene, and upwards of 30 pounds of carbone; that is to ſay, it is compoſed of water and carbone; with an exceſs of oxigene. It is not this whole compound which enters into the formation of the oxalic acid; it is decompoſed, as well as the nitric acid which is uſed in its preparation: and without being under the neceſſity of oppoſing to Mr. Kirwan, who does not deſcribe any particular experiments on this head, eſſays

made

made with all the required accuracy, which are ſtill wanting, we have ſufficient data to prove to him, that our theory is as ſimple on this head as on all the others, and that it has not, like his, the diſadvantage of requiring multiplied ſuppoſitions.

When ſugar is combined with the nitric acid, there is diſengaged, during the effervescence, a conſiderable quantity of carbonic acid mixed with nitrous gas; this acid cannot ariſe but from the charcoal of the ſugar united to the oxigene of the acid of nitre, for this laſt never affords it, excepting when in contact with charcoal, or ſome matter which contains that ſubſtance, and proportional quantities of charcoal and nitric acid may be totally converted into nitrous gas and carbonic acid; this firſt fact proves that the oxalic acid, which is formed in proportion as the carbonic acid gas and nitrous gas are diſengaged, contains leſs carbone than the ſugar, and explains why this laſt loſes weight by becoming acid; the oxalic acid may therefore be conſidered as a mixed acid, formed of hydrogene, carbone, and oxigene, in certain proportions not yet determined. That the oxigene does not form ſimply water with the hydrogene, and carbonic acid with the carbone, but a new and peculiar compound; it is becauſe theſe two principles are united together in a peculiar manner, and adhere equally to the oxigene. As ſoon as a foreign force comes to break the

equilibrium, ſuch, for example, as the action of a certain degree of heat, the three principles are ſeparated, and will unite together in another order; the hydrogene will be diſengaged, and the carbonic acid will be formed, which did not exiſt before; ſuch, likewiſe, are the products of diſtillation of this acid. As the oxalic acid is compoſed of two of the ſubſtances which have the greateſt poſſible affinity with oxigene, moſt part of the metals cannot decompoſe it; beſides which, as zinc and iron, which alone are capable of depriving this acid of part of its oxigene, require for that purpoſe a conſiderably ſtrong temperature, this laſt would decompoſe the oxalic acid by effecting the re-action of its principles and the rupture of their equilibrium, ſo as to alter them very much.

Nothing more is wanting to afford us a more accurate knowledge of the oxalic acid, than to aſcertain exactly the proportion of the principles which enter into its compoſition; which may be done by attending to the ratio of the products of the diſtillation of ſugar, of its fermentation, and of its analyſis by the nitric acid. The condenſation of its principles is likewiſe an element to be ſought after in this enquiry; and the ſpecific heat and gravity may indicate this.

Our doctrine upon this point, as well as upon all others, is merely the ſimple reſult, pointed out by experiment. It agrees with

all

all which is known concerning this oxalic acid, and all the materials which afford it by the action of the nitric acid. The whole of theſe, in the laſt analyſis, will ever be reduced into hydrogene, oxigene, and carbone.

We think, likewiſe, after theſe general data, that the ten different vegetable acids, at preſent known, all contain the ſame principles as the oxalic acid, viz. carbone, hydrogene, and oxigene; but that they differ from each other in the proportion and condenſation of theſe principles, as well as in the addition of ſome other ſubſtance, ſuch, for example, as a ſmall portion of alcohol in the acetous acid. This opinion is founded on the convertibility of theſe acids into each other, which is proved by the reſearches of Meſſrs. Crell, Hermſtad, &c. and is effected ſimply by the change of the quantity of their component parts.

SECT. IX.

Of the Calcination and Reduction of Metals, and the Formation of Fixed Air.

TO calcine a metal is to deprive it of its metallic ſplendor, or reduce it to a brittle, leſs coherent and pulverent form: malleable metals thereby loſe their malleability, and mercury its liquidity. To reduce a metal is to reſtore to it the metallic luſtre, and the degree of coherence and malleability that are peculiar to it.

Metallic calces are *heavier* than the metal of which they are formed, and hence are evidently united to ſome new ſubſtance; but they are ſpecifically *lighter* than before calcination, and hence this new ſubſtance is lighter than that to which they were united before calcination, if they were united to any.

The different ſubſtances, by whoſe means in different degrees of heat, different metallic ſubſtances may be calcined, are reſpirable air, water, acids, alkalis, mercury, with the aſſiſtance of reſpirable air, and various other metallic ſubſtances in different circumſtances.

According to the new theory, metallic ſubſtances loſe no peculiar ſubſtance during calcination,

cination, but barely take in, and unite to the oxigenous principle, that is, pure air deprived of the greater part of its ſpecific heat.

Thoſe who admit the exiſtence of the inflammable principle in metals, are moſtly agreed, that during calcination it is ſeparated from them; but with regard to the new ſubſtance which metals take in, few of the preſent adherers to the old ſyſtem have as yet declared their ſentiments. I ſhall forbear entering on a diſcuſſion of antiquated opinions long ago exploded, and alſo of that of Mr. Scheele, which has ſcarcely been embraced by any body, and has been ſufficiently refuted by Mr. Lavoiſier, and the experiments of Dr. Fordyce.

Mr. Cavendiſh inclines to think that the imperfect metals loſe their principle of inflammability or phlogiſton, during calcination, and take in water in its ſtead. But with reſpect to the calces of mercury (and of the perfect metals) he thinks it ridiculous to decide, whether the mercury, and not the water, or the water, and not the mercury, have loſt the principle of inflammability.

Hence, in the antiphlogiſtic ſyſtem, to reduce a calcined metal, is barely to deprive it of the oxigenous principle; and in that of Mr. Cavendiſh, it is in moſt caſes barely requiſite to decompoſe the water to which the calx is united; the inflammable principle of the water uniting to the metal and the pure air, its other ingredient being ſet looſe.

In my opinion, metallic ſubſtances by calcination, loſe their phlogiſton, which is nothing elſe but pure inflammable air in a concrete ſtate, and at the ſame time unite moſt commonly to fixed air, formed during the operation; but ſometimes ſome of them unite to water and other ſubſtances, by whoſe means they are calcined. The calces of the perfect metals may therefore be reduced by the decompoſition of their fixed air, and thoſe of the imperfect, and ſemi-metals, partly by the decompoſition of their fixed air, and partly by its expulſion, and that of the other foreign bodies they had abſorbed, and their ſimultaneous reunion to the inflammable principle.

To ſubſtantiate this opinion, it is neceſſary to prove, that phlogiſton, or inflammable air in a concrete form, exiſts in metallic bodies endowed with their metallic ſplendor and peculiar coherence. This, I flatter myſelf, I have ſufficiently performed on another occaſion*. I have there ſhewn, 1ſt. That many metals, during their ſolution in acids, produce inflammable air; yet that the ſame metals placed in the ſolution of other metals in the ſame acids, though they are diſſolved, yield no inflammable air; but at the ſame time, and in the ſame proportion, the metal before diſſolved and calcined, is reſtored to its metallic luſtre; from whence I inferred, that the ſubſtance which the

* Phil. Tranſ. 1782, p. 195.

added

added metal would, if alone, give out in the form of inflammable air, is, on this occaſion, imbibed and abſorbed by that which is reſtored to its metallic luſtre.

2dly. That metallic calces are reduced to metals, by merely heating them in inflammable air; which they viſibly abſorb. 3dly. That inflammable air has been expelled from them *in vacuo*, by mere heat, at leaſt with the aſſiſtance of moiſture. And 4thly. That imperfect metallic ſubſtances are never reſtored to their perfect metallic ſtate, but by ſubſtances that contain the inflammable principle. I ſhall, therefore, now do little more than reply to the objections that have been made to the general concluſion, and to my theory of fixed air, by whoſe decompoſition the calces of mercury are revived.

In the firſt place, the antiphlogiſtians contend that the inflammable air produced during the ſolution of metals, proceeds from the decompoſition of water. "For" (ſays that eminent mathematician and philoſopher, Mr. de la Place, who firſt ſuggeſted this improvement on the antiphlogiſtic ſyſtem) "by the action of "acids the metal is calcined, that is, united to "vital air." Theſe expreſſions are not yet allowed to be ſynonimous. "That no part of "the vitriolic acid is altered by iron, appears "by Mr. Lavoiſier's experiments, who found "it to ſaturate the ſame quantity of alkali as "before." This, if admitted, only proves that the

the inflammable air does not proceed from the acid. " If the inflammable air originated from " the metal, we ſhould obtain it likewiſe by " means of the nitrous acid." By no means; the nitrous acid is evidently decompoſed, the inflammable air unites to its baſis, and forms nitrous air. " If it formed nitrous air, it ſhould " appear on uniting nitrous air with pure air." No, it unites to the pure air, and forms fixed air. " Moreover the action of nitrous acid " on mercury, developes nitrous air, yet it " does not appear that the mercury imparts " inflammable air, ſince the reſulting calx of " mercury is revived without the addition of " inflammable air." This revivification has been explained at large, at the end of the fourth ſection. That it is due to inflammable air will again be ſeen in the ninth *.

And

* NOTE received from Mr. De la Place, by the French Tranſlator—

I ſhall anſwer the objections of Mr. Kirwan, by reſuming my reaſoning upon the decompoſition of water in metallic ſolutions.

Metals are calcined by the action of acids, and unite in this operation to oxigene; this is inconteſtible from all the late experiments on this head. In the ſolution of iron by the ſulphuric acid, the acid is not altered, becauſe it can always, as well before as afterwards, ſaturate the ſame quantity of alkali. The inflammable gas which is diſengaged, and the oxigene which combines with the iron, do not therefore come from the acid; and ſince the ſolution equally takes place in cloſed veſſels, it is clear that the water alone affords the vital air neceſſary to this operation. It therefore produces the inflammable gas which is diſengaged, becauſe when it parts with one of its principles, the other is ſet at liberty. To this Mr. Kirwan makes no reply.

And in effect, if we conſider the decompoſition of water in this caſe, in a chymical point of view, it cannot but appear exceeding improbable; every decompoſition ariſes either from a ſingle or double affinity; therefore, if during the diſſolution of iron in the dilute vitriolic acid,

The inflammable gas affords a ſecond proof of the decompoſition of water in theſe ſolutions, for we have ſeen that it is not afforded by the ſulphuric acid. If we ſuppoſe it to be produced by the iron, it ought to be equally obtained by the action of the nitric acid; but it is known that, in this caſe, nitrous gas only is diſengaged. It may indeed be ſaid, that it is one of the principles of nitrous gas; but it ought to reappear, when, by uniting nitrous gas to vital air, the decompoſed nitrous acid is formed again.

Here Mr. Kirwan replies, that in this union fixed air is formed, which, according to this excellent philoſopher, conſiſts of vital air and inflammable gas; but all the attempts which have been made to aſcertain the exiſtence of fixed air in this experiment, have not ſhewn the ſmalleſt traces of it.

To prove, moreover, that nitrous gas does not contain inflammable gas as a principle, I will add, that this gas is developed by the action of nitric acid upon mercury, though this metallic ſubſtance does not contain inflammable gas, as is proved by the reduction of its oxide, without its intermedium, and by the ſimple action of heat. Mr. Kirwan replies, that in the oxidation of mercury, the inflammable gas combines with vital air, and forms fixed air, which unites to the mercurial oxide, and then, in the revivification of this oxide, the fixed air reſtores its inflammable principle to the mercury, and diſengages the vital air. Mr. Kirwan appears therefore to admit, that the inflammable gas remains in combination with the mercurial oxide in the oxidation of this metal by the nitric acid. Whence it follows, that it does not enter into the formation of the nitrous gas which is developed. Thus we ſee, that the production of oxigene and of inflammable gas, in the ſolution of iron by the ſulphuric acid, concur in ſhewing that the water is decompoſed in this operation.

water

water is decompoſed, this muſt happen either by virtue of a ſingle or of a double affinity; yet neither can be ſaid to take place: Not a double affinity, ſince the inflammable air eſcapes without uniting to the acid; not a ſingle affinity, ſince there is no proof that any ſuch affinity exiſts in this caſe, and if it did exiſt, water ſhould as eaſily be decompoſed by iron without an acid, as when an acid is preſent, or rather more eaſily, ſince the affinity of water to the acid muſt diminiſh its tendency, or that of any of its component parts, to unite to any other ſubſtance, and on that account we find a variety of ſolutions precipitated by the vitriolic acid, merely becauſe it attracts the water neceſſary to hold them in ſolution*. I would be glad to know what part the acid acts here; in the new theory it ſeems to be quite idle, and contributes nothing to the ſolution. Why does not its oxigenous principle unite to the inflammable air of the water, at the ſame time that the oxigenous principle of the water unites to the metal? ſince, by the table of Mr. Lavoiſier, this principle has a greater affinity to inflammable air, than to ſulphur. How comes it that volatile vitriolic acid diſengages inflammable air from iron? ſince its own oxigenous principle is ſufficiently developed, and ſufficiently copious to unite to iron, without

* As tartar, vitriolate, alum, &c. See 1 Mem. Sçav. Etrang. p. 105, and Vogel, § 769.

having

having recourſe to that of water. How does fixed air expel inflammable air from iron? Do all acids help the decompoſition of water, and yet remain inert?

Beſides, though iron and zinc are the only metals which by Mr. Lavoiſier's table have a greater affinity to the oxigenous principle, than inflammable air has to that principle; yet inflammable air is alſo ſet looſe during the ſolution of other metals, which by that table have a weaker affinity to the oxigenous principle than inflammable air has to it. Thus inflammable air is produced by the ſolution of manganeſe in the dilute vitriolic acid *, and by the ſolution of tin in the marine acid; by this table alſo vitriolic acid and charcoal ſhould decompoſe water, in the ſame circumſtances in which vitriolic acid and iron decompoſe it, which yet is not pretended.

I am very ſenſible that all general reaſonings ſhould give way to *facts*; but ſurely, when adduced againſt *mere inference and conjecture*, they muſt have their due weight.

To deſtroy this ſuppoſition ſtill more effectually, I made the following experiment: Having heated ſome pounds of mercury to † 212°, and kept it in that heat for 6 hours, often ſtirring it to diſſipate all moiſture, I amalgamated one pound of it by frequent agitation with 360 gr. ‡ of filings of zinc, which had been previouſly

* 2 Bergm. 210. † 80° Reaumur,

‡ 439,2 gr. poids de marc.

viouſly heated nearly to redneſs, in a dry glaſs bottle, and poured the whole, with about 40* gr. more of zinc ſtrewed over its ſurface, into a coated glaſs retort made as dry as poſſible, and which with its adopter contained about 20† cubic inches. I then diſtilled the whole with a gentle heat, and received the air in 5 portions over mercury: the firſt and ſecond portions, each about 5 cubic inches, were common air; the third, nearly 5‡ cubic inches, was inflammable air, and detonated with common air; the 4th, alſo about 5§ cubic inches, made 4 ſucceſſive exploſions, after which a conſiderable abſorption took place, and the mercury began to diſtil over; a fifth portion of air paſſed ſlowly, $\frac{1}{2}$ of which was fixed air, and the other $\frac{1}{2}$ ſlightly reddened with nitrous air.—In this experiment, the faireſt I could deviſe, moiſture was avoided as much as poſſible, and none could be preſent, but that included in the air neceſſarily abſorbed during the amalgamation: the inflammable air ſeems then to have proceeded from the zinc, which, like all other imperfect metals, is in ſome meaſure calcined during its union with mercury, and thrown into an aerial form by the heat applied, when there was but little common air in the retort: this air had a very peculiar ſmell.

It is true that vitriol of iron, when diſtilled,

* 48,8. † 16,52 French inches. ‡ 4,13. §4,13.

gives

gives at laſt dephlogiſticated air; but this air evidently proceeds from the decompoſition of part of the acid, and not from that of the water; for its production is always preceded by a large quantity of vitriolic air*, ariſing from the abſorption of part of the fixed air of that acid, by the metallic calx.

To prove the decompoſition of water, Mr. Lavoiſier made the following experiments: 1ſt, He let up a mixture of water and filings of iron, into a tube filled with mercury, and in a few days obtained a ſmall quantity of inflammable air. 2dly. Having paſſed the ſteam of boiling water through a red hot iron tube, he obtained a large quantity of inflammable air; the inner ſurface of the tube was calcined, and had the appearance of what is called the *ſpecular*, or *teſſular iron ore*, of great hardneſs, ſcarcely magnetic, and affording no air with acids†. The iron increaſed in weight from 25 to 30 per cent.

Theſe experiments ſeem to me to prove nothing more than that water unites to iron, and expels inflammable air from it, which is further confirmed by the following conſiderations: If a little water be thrown on a large heap of filings of iron, a conſiderable heat is ſoon produced‡, which appears to proceed from the condenſation of the water while uniting to the

* 4 Prieſtley, 216. 220. † Mem. Par. 1781. p. 271, 272, and 487. ‡ 3 Bergm. 94.

iron;

iron; the heat given out, exceeding that abſorbed by the inflammable air, whoſe weight is exceeding ſmall. In Mr. Lavoiſier's hypotheſis, it is only the oxigenous principle of the water which is abſorbed by the iron; and as this is already exceedingly condenſed in water, it does not appear to me likely to give out much heat. 2dly. This calx is very different from that formed by the abſorption of air, ſuch as ruſt; for fixed air may be extracted from this, and even dephlogiſticated air; but no air of any ſort can be extracted from iron calcined by water.

Dr. Prieſtley has alſo made many curious experiments on this ſubject, which deſerve particular attention, as their reſults are incompatible with the new theory, and ſet the abſorption of water *in ſpecie*, beyond contradiction. By the help of a burning glaſs he heated a bit of iron in dephlogiſticated air, extracted from precipitate *per ſe*, and preſently perceived the air to be diminiſhed, and viſibly abſorbed by the iron, which was converted into a ſlag, and gained a weight very nearly correſponding to that of the air which was abſorbed; but when he afterwards heated this ſlag in inflammable air, the inflammable air alſo diſappeared, a conſiderable quantity of water was produced, the iron recovered its metallic ſtate, and loſt a weight nearly equal to that of the water it had given out*. In

* 6 Pr. 73—85.

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the firſt experiment the phlogiſton of the iron united to the dephlogiſticated air, and formed water, which the iron abſorbed, became a ſlag, and muſt thereby have gained the weight of the dephlogiſticated air. In the ſecond experiment the water was expelled, and converted into vapour, while the inflammable air was abſorbed, and the iron thereby reſtored to its original ſtate and weight. In the antiphlogiſtic hypotheſis it muſt be ſaid, that in the firſt experiment the pure air united to the iron, and formed a ſlag; but in the ſecond, the dephlogiſticated air quitted the iron, united to the inflammable air, and formed water: but this contradicts Mr. Lavoiſier's table, where pure air is repreſented as having a ſtronger affinity to iron than to inflammable air; nor can heat be ſaid to be the cauſe of the expulſion of pure air from iron, and its reunion to inflammable air, ſince this expulſion takes place in the very circumſtance in which water is ſaid to be decompoſed by the avulſion of the oxigenous principle from inflammable air, and the union of the oxigenous principle to iron: if it be replied that we alſo aſſert that water is expelled from iron by inflammable air, in the very circumſtance in which we before aſſerted that inflammable air was expelled from it by water, I ſhall anſwer that the circumſtances are not the ſame; when water expels inflammable air from iron, the water contains much more ſpecific heat

than either iron or its phlogiſton, and the phlogiſton has room to eſcape in the form of inflammable air; but when inflammable air expels water from iron, the inflammable air is confined, and having an equal affinity to iron, and more ſpecific heat than the condenſed water, and preſſing upon the iron with conſiderable force by reaſon of its heat and confinement, it gives out its heat to the water, which is immediately converted into vapour, and condenſed on the ſides of the glaſs. In the antiphlogiſtic hypotheſis this reaſon will not apply, becauſe according to it, the oxigenous principle has a ſtrong affinity to iron, and the inflammable air none at all; ſo that there is no ſubſtance at all that tends to expel the former, and the communication of ſpecific heat to the oxigenous principle, ſhould rather impede than promote its union with the inflammable, ſince this heat muſt be given out before that union can take place.

If the above mentioned ſlag (that is, iron calcined by the ſteam of water) be mixed with charcoal perfectly dried, and out of which all looſe inflammable air has been expelled, and then diſtilled in an earthen retort well baked and glazed on the outſide, fixed and inflammable air will be produced, and the iron reduced to its metallic form*. Here I aſk from whence the inflammable air proceeded? The

* 6 Prieſt. 109.

anti-

antiphlogiſtians cannot ſay it proceeds from the charcoal, for they deny it to contain any; nor can they have recourſe to the decompoſition of water; for, according to them, the ſlag contains the oxigenous principle ſingly, and not water: this deciſive argument is urged againſt them by Dr. Prieſtley.

The next ſet of experiments, which Mr. Lavoiſier adduces in proof of the decompoſition of water, are thoſe which he made on charcoal, which I ſhall examine in conjunction with thoſe of Dr. Prieſtley, on the ſame ſubject.

Mr. Lavoiſier placed * 248,62 gr. troy of charcoal, out of which all adventitious air and moiſture had been expelled, in an iron tube lined with copper (water having no action on copper); and having paſſed through it the ſteam of boiling water, to the amount of 1122 † gr. the reſult was that 6644 ‡ cubic inches of inflammable air were produced, whoſe weight he eſtimates at § 550 gr.: by introducing a cauſtic alkali, he found ¼ of the bulk of this air to conſiſt of fixed air, and there remained ‖ 5 gr. of aſhes: as the weight of this product was more than double that of the charcoal employed, he infers that the water muſt have been decompoſed; its inflammable principle forming the inflammable air, and its oxigenous principle uniting to the charcoal, forming the fixed air ¶.

* 303,316. † 1368,84. ‡ 5487,984. § 671.
‖ 4,13. ¶ Mem. Par. 1781, p. 280.

On this experiment I remark, 1ſt. That Mr. Lavoiſier ſuppoſes that the inflammable air and fixed air here produced, were free from water, a ſuppoſition, which neither Mr. Sauſſure's experiments, nor my own, can allow; and if we ſuppoſe that above $\frac{1}{5}$ of the weight of theſe airs was water, a ſuppoſition fully juſtified by my experiments, there will be no neceſſity for inferring that water was decompoſed, but only the charcoal, which was reſolved in great meaſure into its conſtituent principles, inflammable air and fixed air; and even this reſolution is not quite perfect, the inflammable air being ſtill combined with a quantity of fixed air, as appeared by its weight, and its burning with a blue flame.

2dly. I obſerve that the iron tube was not ſo completely coated, as to prevent the iron from being calcined*; ſome part therefore of the inflammable air muſt have been derived from the iron; therefore no calculation founded on this experiment can be concluſive.

3dly. The weight of the fixed air (ſuppoſing it to make $\frac{1}{4}$ of the whole volume of the air obtained) muſt have exceeded that of the whole; for the whole is ſaid to have weighed but 550 gr. but the fixed air amounting to $\frac{6644}{4} = 1661$ cubic inches, ſhould weigh

* Mem. Par. 1781, p. 280.

772 gr. eſtimating 100 cubic inches at 46,5 grains*.

Dr. Prieſtley in making ſimilar experiments found conſiderable variations in the reſults†. When he paſſed no more water than was ſufficient for the production of the air, he never found any uncombined fixed air; but the whole was inflammable air. When a greater quantity of water was uſed, the uncombined fixed air conſtituted from $\frac{1}{12}$ to $\frac{1}{7}$ of the whole: the inflammable air was more than $\frac{1}{8}$ lighter than common air, 100 cubic inches of it weighing 14 grains‡.

In the experiment he moſt depended upon, he found that 94 gr. of charcoal, from which all uncombined air had previouſly been expelled by heat, afforded, by the help of 240 gr. of water, 294 gr. of air, or 1591 cubic inches, $\frac{1}{4}$ of which by bulk, was fixed air§. However, as this weight was not deduced from a direct experiment, no great ſtreſs can be laid upon it, as the Doctor himſelf allows: it muſt be remembered that charcoal perfectly ſtripped of its adventitious air, rapidly re-attracts it, and therefore cannot be exactly weighed, and

* In French numbers the $\frac{5487,984}{4} = 1371,996$ inches at 68,715 gr. the 100 inches make 842,767 gr. which is much greater than 671 gr.

† 6 Pr. 95.

‡ 100 French cubic inches would weigh 20,67 grains.

§ 114,68 gr. of charcoal with 298,8 of water, produced 358,58 gr. or 1314,166 cubic inches of air.

after being weighed, ſtill continues to attract more of it: and if to this cauſe of inaccuracy we add the weight of the air of the veſſels, and of the water abſorbed, we may well account for the great exceſs of weight of the air obtained, over that of the charcoal.

Theſe are all the experiments hitherto adduced to prove the decompoſition of water; and we have ſeen that when well conſidered they have no ſuch tendency, but only prove the power that ſteam has of decompoſing both charcoal and iron, and of uniting in great plenty with the air produced from the former, and when no more water is uſed than is barely neceſſary, the air produced ſeems to be nothing elſe but charcoal itſelf in an aerial form, united to a quantity of water: but the following experiments ſhew that charcoal is compoſed of inflammable and fixed air.

1ſt. Mr. Scheele diſtilled cauſtic fixed alkali with charcoal, and obtained inflammable air, at the ſame time that the alkali became effervescent.

2dly. I heated about ½ an ounce of dry powdered charcoal to redneſs, in a ſmall looſely covered crucible, which it nearly filled, for ſeveral hours; the cover had a hole, through which the air produced might iſſue. I found it to yield inflammable air, which burned with a blue flame during the whole time, which I tried, by firing it from to time to time with a lighted paper; it is impoſſible to aſcribe

cribe this continual flow of inflammable air to any foreign quantity of it which the charcoal might contain.

The ſecond proof which I alleged in favour of the exiſtence of phlogiſton in metals, was deduced from the reduction of their calces to a metallic ſtate, when heated in inflammable air, and the concomitant abſorption of that air: to elude this proof, Mr. Lavoiſier replied, that metallic calces, when heated, give out pure air, and that this air meeting the inflammable air, formed water. As moſt of theſe calces were heated to redneſs in Dr. Prieſtley's experiments, I allow water to have been formed by part of the inflammable air, while another part united to the calces, and therefore this experiment is not now as concluſive as it was when I alleged it, the compoſition of water being then unknown; but the experiment of Mr. Pelletier ſtill ſupports the concluſion, as there is no reaſon to think that water can be formed by the union of inflammable and pure air in the temperature of the atmoſphere.

That metallic calces are immediately united to pure air, is admitted by many, who yet are of opinion that metals contain phlogiſton: yet this admiſſion ſeems to me inconſiſtent with the latter opinion; for they allow that metals during their calcination give out phlogiſton, and that they are incapable of calcination in any other than pure air; this air

therefore meets the phlogiſton, and muſt, with it, form either fixed air or water, one or both of which are abſorbed by the calx, and augments its weight.

Calcination *by fire*, is performed in a low heat below redneſs, or in a red heat. Maſſicot, minium, precipitate *per ſe*, and ruſt, are formed in low heats, and conſequently contain fixed air, and ſome water which they imbibe after calcination; but litharge, flowers of zinc, iron ſcales, which Dr. Prieſtley calls finery cinder, being formed in a red heat, abſorb the water formed during their calcination, and ſome fixed air alſo: the metallic ſubſtances that abſorb fixed air, will (according to the affinity of the metal to phlogiſton) decompoſe either the whole, or the greater part of that air, when they are heated to a higher degree than that at which they abſorbed it; and in an exceeding high degree of heat, as that to which calces of iron are expoſed, in the focus of a burning glaſs, it may poſſibly happen that even the water they contain may be decompoſed. This theory appears to me deducible from the following phænomena.

1ſt. Maſſicot, and the grey calx of lead when moiſtened and heated, give out no other but fixed air, as Dr. Prieſtley aſſures us. When dry, I found them rather to abſorb air by undergoing a further calcination.

2dly. Minium alſo gives out a large portion of fixed air, about $\frac{1}{4}$ of its whole aerial contents,

tents, as Mr. Lavoiſier owns; and to this air it ſeems to owe its colour, which it loſes the inſtant it is deprived of it, and regains when it recovers it, as Mr. Abich has ſhewn. It does not derive it from either flame or ſmoke: for by Mr. Abich's experiments, that which is formed without contact of either, is much redder, and more perfect, than that formed in a reverberatory furnace*.

It has been ſaid that minium, newly made, affords no air at all: to try this, I made ſome ounces of it, and in fact neither by diſtilling it with or without water, could any air be obtained; on the contrary, it abſorbed air, and was converted into litharge and glaſs, and paſſed through the retort; but we muſt not infer from thence that it contains no air, for having mixed 120 gr. of the ſame minium with 18 of ſulphur, I obtained 14 cubic inches of vitriolic air. The former experiment therefore proves no more, than that no air can be expelled from any ſubſtance until it has abſorbed ſome moiſture, of which we have a clear proof in the caſe of native aerated baroſelenite, which will ſooner vitrify than yield any air, though acids expel fixed air from it very readily.

3dly. Ruſt is well known to yield no other than fixed air, and precipitate *per ſe* yields ſome traces of it†.

* 1 Chym. Annal. 1784, p. 400, and 407. † 2 Pr. 217. 3 Pr. 16, and poſt p.

Thence

Thence if marine acid be digeſted with minium, or precipitate *per ſe*, it becomes dephlogiſticated, as it takes up fixed air and parts with a portion of its own phlogiſton to theſe calces: but if it be diſtilled over calces that contain chiefly water, as the calces of zinc, antimony, litharge, or iron, it does not become dephlogiſticated, or only in a very ſlight degree*, which ſhews the great difference between theſe calces and the former.

It is impoſſible to ſuppoſe, that metallic calces formed in the dry way, ſhould give out any more than a ſmall quantity of fixed air undecompoſed, if we allow that the affinity of metallic ſubſtances to phlogiſton increaſes when they are expoſed to a very ſtrong heat; and this we have ſtrong reaſon to believe, ſince ſcarce any of them are reducible by contact with phlogiſtic ſubſtances, but in a ſtrong heat, and the moſt perfect calces of iron are in ſome meaſure revived in the focus of a powerful lens.

The only proof therefore which can be expected that calces formed in the dry way in a low heat, contain no other but fixed air, is, that the quantity of this air ſhould be greater, when the calces can take phlogiſton from ſome other ſubſtances, or at leaſt have their decompoſed fixed air recompoſed by the phlogiſton

* 1. Hermſt. 176.

of

of ſome other ſubſtance, and of this we have ſome inſtances.

1ſt. Mr. Hermſtadt has ſhewn, that the black calx of manganeſe gives abundance of fixed air when diſtilled with certain proportions of iron or zinc *.

2d. From 1 ounce of red precipitate, and 1 of filings of iron, Dr. Prieſtley obtained † 38 cubic inches of fixed air, of which not above ‡ 5 remained unabſorbed by water; and the reſult was equally concluſive when he uſed braſs or zinc inſtead of iron, or turpeth mineral inſtead of red precipitate §. Mr. Scheele and Mr. Cavendiſh alſo obtained a conſiderable quantity of fixed air by this method ‖.

My ſucceſs in repeating this experiment was ſomewhat different; from a mixture of 300 gr. of iron newly filed, and 240 of red precipitate, I obtained no air at all; on the contrary, there was a conſiderable abſorption. Thinking that water might be neceſſary, I repeated this experiment, uſing precipitate *per ſe* inſtead of red precipitate, and varying the proportion. From 240 gr. of this and 120 of newly-made filings of iron, diſtilled in a very ſmall coated glaſs retort, and ſprinkled over with water, I

* Hermſtadt, 277.

† From 586 gr. of red oxide of mercury, and 586 gr. of iron filings, 31,588 cubic inches of carbonic acid gas were obtained.

‡ 4,13. § 6 Pr. 253. ‖ 1 Chym. Annal. 1785, p. 154.

got 4,5 cubic inches of fixed air, and 36 of a mixture of dephlogiſticated air and inflammable air: the iron after the operation weighed 1,4 grains*.

Mr. de la Metherie, from equal parts of filings of iron and red precipitate obtained only the air of the veſſels; and from 2 ounces of red precipitate and 1 drachm of filings of iron, he obtained a ſmall quantity of fixed air, the greater part being dephlogiſticated†. I believe much to depend on the ſize of the retort and the purity of the filings: when the retort is large, there is air enough to calcine the filings to ſome degree before the precipitate is decompoſed; if ſmall, the fixed air unites to the iron in proportion as it is formed. In my laſt experiment it appears that water unites to iron more readily than fixed air does, and that mercury decompoſes its own air more readily than it takes up inflammable air, as being more intimately united to it, and as it is already condenſed.

240 gr. of *lead*, and 240 of red precipitate, afforded me no air; the lead was calcined for the moſt part.

400 gr. of *tin*, and 460 of red precipitate, inflamed in the retort and burſt it.

* In French numbers 292,8 gr. of red oxide of mercury, and 146,8 gr. of iron produced 3,717 inches of acid gas, and 19,736 of oxigenous, and hydrogenous gas. The iron afterwards weighed 175,68 gr.

† 27 Roz. 146.

240 gr. of *biſmuth*, and the ſame quantity of red precipitate, diſtilled with a very low heat, afforded only five cubic inches of air, of which two were fixed air. The ſame mixture diſtilled with a rapid heat, afforded 19 cubic inches of air, of which one was fixed air, the remainder ſomewhat better than common air*: the biſmuth was converted into litharge.

240 gr. of *zinc*, and the ſame weight of red precipitate, being treated in the ſame manner, the zinc ſublimed, ſtopped the neck of the retort, inflamed and broke it. The ſame mixture, in a larger retort, and ſlower heat, produced no air. 60 gr. of the reſiduum, mixed with 240 of red precipitate, inflamed and burſt the retort.

200 gr. of copper, and 240 of red precipitate, gave no air, though the mercury diſtilled over.

Hence it appears, that in ſome caſes, particularly when water is uſed, a quantity of fixed air paſſes undecompoſed, but that in general mercury decompoſes its own fixed air, and the dephlogiſticated air produced, unites to the naſcent inflammable air of the metals with which it comes in contact, and is abſorbed by them.

* In French numbers 292,8 gr. of biſmuth, and an equal quantity of red oxide of mercury produced 4,13 cubic inches of air. The ſame mixture diſtilled at greater heat afforded 15,694 gr.

Calces formed in the moiſt way by water, or amalgamation, afford much clearer proofs of the principles of fixed air, and that this air or water are the only ſubſtances that metals take up in calcination.

On the 22d of June, 1785, I put 3 ounces of filings of *lead*, and ½ an ounce of diſtilled water, into a glaſs bottle, whoſe capacity was 433 cubic inches, and cloſed it with a glaſs ſtopper; in a few days the ſurface of the lead became white. I agitated it from time to time; after a few weeks, I with much difficulty opened the bottle to let in more air, and on the 5th of September I withdrew the contents, of which the greater part was calcined, and ſeparating this part from the reſt, by the help of a large quantity of diſtilled water, I evaporated it to the conſiſtence and colour of ſtarch, but ſomewhat bluer, and then diſtilling 472 gr. of it, obtained 24 cubic inches of fixed air, with ſcarce any reſiduum: what remained in the retort was converted into litharge*.

A quantity of filings of *iron*, treated in the ſame manner, afforded no air at all.—From *zinc* calcined in this manner, I obtained ſome fixed air, but by accident the greater part of it was loſt.

* 1758 gr. of lead with 293 of water, were oxided in a veſſel whoſe capacity was 357,658 cubic inches: 675,62 gr. of this oxide afforded by diſtillation 19,826 cubic inches of carbonic acid gas.

N. B.

N. B. The water in which zinc had been calcined, became ſapid, and with aerated fixed alkali, afforded a precipitate; but Pruſſian alkali produced no change in it.

Again, having made an amalgama of ſome pounds of mercury, and 300 gr. of zinc, by ſhaking them in a large bottle with ſome diſtilled water, and leaving ¼ of the bottle empty, I ſeparated 857 gr. of a whitiſh-grey calx, and by diſtillation procured from it 15 cubic inches of fixed air*. When this ceaſed to be produced, and an abſorption began to take place, I admitted more common air, but after ſome time the zinc inflamed, which ſhews that ſome part of it remained uncalcined.

From a black powder, obtained from a ſimilar treatment of 480 gr. of lead filings, and ſome pounds of mercury, I obtained 8 cubic inches of fixed air†, and 6‡ of air ſomewhat better than common air. The lead in the retort was partly in the ſtate of maſſicot, partly minium, and the greater part litharge. Dr. Prieſtley, who firſt made this experiment, repeated it ſeveral times with the moſt ſcrupulous attention, and conſtantly obtained a large portion of fixed air, and at the end ſome dephlogiſticated air §.

Theſe experiments induce me to believe, not only that fixed air is formed during the

* 1045,54 gr. of the amalgam of zinc, oxided in water, produced 12,39 cubic inches of carbonic acid gas.

† 6,608. ‡ 4,956. § 6 Pr. 256.

calcination

calcination of metals, and abſorbed by them, but alſo that its conſtituent principles are dephlogiſticated air and phlogiſton. As an analytical confirmation of this opinion, I ſhall mention the two following experiments.

1ſt. Mr. Hermſtadt having exhauſted a quantity of manganeſe of all its pure air, by a ſtrong and long-continued heat, he placed it in an earthen tube, and heating this tube to redneſs, he paſſed through it 150 cubic inches of fixed air 8 times, at laſt it became ſo pure, that it admitted a candle to burn in it, and many white ſpots appeared in the manganeſe*.

2dly. Mr. Monge having taken the electric ſpark in fixed air, found, 1ſt. That the air by this operation increaſed in bulk $\frac{1}{144}$, and its volume continued to increaſe even after the electric ſpark ceaſed to be taken in it. 2dly. That the iron conductor was calcined; but this circumſtance need not be conſidered, as the principal effect was the ſame when a conductor of platina, which could not be calcined, was uſed. 3dly. That on expoſing the air after the operation, to cauſtic fixed alkali, 3 parts out of 5 were abſorbed, but the reſiduum was inflammable air†. This experiment he explains thus: 1ſt. All fixed air contains water, and this water increaſes its bulk. 2dly. The mercury being heated by the electric ſpark, decompoſes the water and ſets looſe the inflam-

* 1 Hermſt. 280. † 29 Roz. 277.

mable

mable air. 3dly. The fixed air diſſolves a portion of mercury and water, but when the operation is over, it depoſits it and diſſolves more mercury, and the mercury thus diſſolved increaſes its bulk*. This explanation appears to

* NOTE of Mr. Monge.

As Mr. Kirwan appears not to have clearly apprehended the explanation I have given of the phenomenon he has ſpoken of, I ſhall proceed to give a concife account of it.

A ſlight experience with elaſtic fluids is ſufficient to ſhew, not only that the carbonic acid gas holds water in ſolution, but likewiſe that the quantity of water it diſſolves is much greater than the air of the atmoſphere can abſorb in like circumſtances. In fact, when we cool a veſſel filled with carbonic acid gas, which has been in contact with water, the ſides of the glaſs are covered with a dew which renders them leſs tranſparent, and is much more abundant than that which is obſerved in a ſimilar veſſel filled with atmoſpheric air. Now, when the air of the atmoſphere diſſolves water, ſpirit of wine, ether, &c. its volume is increaſed, and the dilatation it ſuffers is greater in proportion as the ſubſtance diſſolved is more evaporable, and the quantity diſſolved is greater: it is therefore probable that the ſame effect takes place when the carbonic acid diſſolves water, and that if by any means this elaſtic fluid were deprived of all the water it retains, its volume would be ſenſibly leſs under the ſame preſſure, and in the ſame temperature.

Moreover, if the air of the atmoſphere can diſſolve mercury, as Mr. Vandermonde and myſelf have aſcertained by direct experiments, of which we gave an account to the Academy in 1781, it is very probable that the carbonic acid gas can likewiſe hold it in ſolution, and that the volume of this elaſtic fluid is by that means augmented. This indeed is a ſimple induction, not ſupported by any previous experiment; but it agrees ſo well with all the circumſtances of the phenomenon, which is now to be explained, that it may be conſidered as verified by the phenomenon itſelf.

to me very unſatisfactory; for in the firſt place, if the inflammable air and increaſe of bulk

Hence when a ſucceſſion of electrical ſparks are excited in carbonic acid gas, which has been expoſed for ſome time over mercury, and which conſequently holds both mercury and water in ſolution, the ſparks diſpoſe to oxidation the diſſolved mercury which is ſituated between the parts of the excitator; and becauſe the oxigene which is in the diſſolved water adheres leſs to the hydrogene, than that of the carbonic acid gas adheres to the carbone, it is the water which the mercury decompoſes in its tranſition to the ſtate of the black oxide; and the hydrogene of the water, being ſet at liberty, takes the form of an elaſtic fluid. For theſe reaſons the bulk muſt ſuffer two different alterations. 1ſt. It muſt be diminiſhed, becauſe, on the one hand, the mercury is precipitated after its oxidation; and, on the other hand, part of the diſſolved water falls with the mercury in conſequence of its decompoſition. 2. It muſt be augmented by the diſengagement of hydrogenous gas, which is in a ſtate of greater expanſion than when it poſſeſſed the form of diſſolved water; and the abſolute increaſe in the whole volume of the gas conſiſts of the difference between theſe two oppoſite effects. When the carbonic acid gas is thus deprived of the water, and part of the mercury it held in ſolution, it becomes capable of diſſolving more mercury and more water, if the mercury of the apparatus be not entirely deprived of this liquid; and becauſe this ſolution cannot be made but gradually, we obſerve a gradual increaſe to take place in the volume of the gas, after the excitation of ſparks has ceaſed.

It is not therefore the mercury in the liquid ſtate, as Mr. Kirwan ſeems to have underſtood it, which is oxided by means of the electric ſpark, excited at a conſiderably great diſtance from it; this indeed would be difficult to conceive, but it is that which being held in ſolution in the carbonic acid gas, and under the form of elaſtic fluid, is in the vicinity of the ſpark, and directly oppoſed to its action.

Hitherto I have mentioned only one of the cauſes of alteration, which the electric ſpark produces in the volume of carbonic

bulk aroſe from the decompoſition of water by mercury, then inflammable air ſhould equally be produced by taking the electric ſpark in phlogiſticated or dephlogiſticated airs, for theſe alſo contain water; and yet Mr. Cavendiſh could not produce the leaſt alteration by taking the electric ſpark in them. 2dly. The dimenſions of inflammable air were not altered by taking the electric ſpark in it, as appears by the experiments of Dr. Prieſtley and Mr. Van Marum*; yet this air contains more water than any other. 3dly. There is no ſort of proof that mercury is

carbonic acid gas; and if this cauſe alone were attended to, it would be proper to conclude that the water and the mercury it holds in ſolution amount to nearly one third of its volume; which is ſcarcely probable. But it muſt be obſerved that the carbonic acid gas has the faculty, like every other acid, to combine with metallic oxides; the oxided mercury therefore ſeizes a part of this fluid without decompoſing it, and carries it with it in the ſolid form; which is a new cauſe of diminution in the quantity of this gas. It is even very probable that in this phenomenon the preſence of the carbonic acid gas favours the operation of the mercury, and the decompoſition of the water in the ſame manner as the ſulphuric and muriatic acids occaſion the decompoſition of water by iron; a decompoſition which would not take place, at leaſt in ſo evident a manner, without the preſence of theſe acids. From this cauſe it may be explained in a ſimple manner, why the electric ſpark diſengages hydrogenous gas, when it is excited in carbonic acid gas expoſed over mercury, while it is not diſengaged by the ſpark in oxigenous, hydrogenous, and azotic gaſes, though theſe, as well as the former, are capable of holding water in ſolution.

I may add beſides, that I had no other intention than to give a plauſible explanation of a phenomenon, whoſe reſults appeared ſomewhat extraordinary; and it is admitted, that in order to give it a ſufficient degree of certainty, it is neceſſary to verify it by direct experiments.

* 4 Pr. 367. 27 Roz. 151.

ſoluble in fixed air, any more than in phlogiſticated, dephlogiſticated, or inflammable air, whoſe dimenſions remain unaltered; and if fixed air could diſſolve any, and increaſe in bulk, it ſhould ſurely diſſolve more while hot than after the operation, when it becomes cold. 4thly. If fixed air could diſſolve mercury, it does not follow that the bulk of this air ſhould be increaſed, but rather diminiſhed, as Mr. Berthollet found that of inflammable air to be by diſſolving plumbago. 5thly. That mercury ſhould decompoſe water, is contrary to Mr. Lavoiſier's table of affinities, according to which, the inflammable principle has a ſtronger affinity to the oxigenous than mercury has; and let it not be ſaid, that this is only true in low heats, for in low heats neither of them unite to the oxigenous principle, and in very high heats the mercury rather expels than abſorbs that principle. 6thly. It is highly improbable, if not incredible, that the ſurface of the mercury ſhould be ſo heated as to incline to calcination, while the remainder of its maſs is cold.

It ſeems therefore much more probable, that fixed air itſelf is decompoſed in this experiment, and water formed; but as fixed air contains more phlogiſton than water does, part of the phlogiſton is let looſe and the bulk thereby increaſed: the water mixing with the mercury forms the black powder, as Dr. Prieſtley often obſerved. The increaſe of bulk after

ter the operation may ariſe from the re-union of ſeveral ſmall bubbles of air, diſperſed through the mercury during the commotion attending the electric ſpark.

The antiphlogiſtians are of opinion, that fixed air ariſes from the union of dephlogiſticated air with charcoal. An obvious, and in my opinion an inſurmountable objection to this opinion, ariſes from its formation in many caſes where charcoal cannot be ſuppoſed to be preſent; as in the calcination of metals, in reſpiration, in vegetation, &c. Charcoal is no farther concerned than as it contains inflammable air.

Mr. Lavoiſier placed a certain quantity of charcoal in a box, with a bit of tinder and phoſphorus; this box he introduced under a jar filled with dephlogiſticated air, and ſtanding on mercury, and then fired it by means of a red-hot iron: the operation being over, he found the charcoal to have loſt 17,2 gr*. but that 67,1787 gr. of fixed air were produced, and that of the original quantity of dephlogiſticated air, namely, 95,745 gr. only 34,075 gr. remained: but on comparing the weight of the charcoal conſumed, and that of the original quantity of dephlogiſticated air, with that of the fixed air produced, and that of the unconſumed dephlogiſticated air, he found a difference of about 11 gr. which he

* French weight and meaſures are here given.

aſcribes to the formation of water, from the union of ſome aqueous inflammable air remaining in the coal, with part of the dephlogiſticated air*.

This experiment proves no more than that fixed air is formed of the union of dephlogiſticated air with one of the conſtituent parts of charcoal, namely, the phlogiſton or inflammable air, which I have conſtantly contended for, and which all chymiſts, who admit phlogiſton, and that charcoal is a compound of phlogiſton and fixed air, muſt alſo allow; for here the weight of the fixed air produced, is more than triple that of the charcoal employed.

That fixed air is formed, not by the union of dephlogiſticated air with charcoal in the aggregate, but with the inflammable air it contains, appears from the experiments of Dr. Prieſtley; for having driven the ſteam of water through charcoal in a red hot earthen tube, he obtained a large quantity of inflammable air, together with ſome uncombined fixed air, as already mentioned: but after ſeparating this fixed air, taking the electric ſpark in a mixture of this inflammable, with an equal bulk of dephlogiſticated air, he produced a bulk of fixed air ſuperior in weight to the inflammable air employed †; ſo that here, either fixed air is formed, or fixed air is pre-contained in this

* Mem. Par. 1781, p. 448. † 6 Pr. 97. 172.

inflammable

inflammable air and ſet looſe, while the real inflammable part is converted into water, and cauſes the increaſe of weight, which I am inclined to think is what really happens, and confirms the opinion I advanced in p. 178; but if this fixed air pre-exiſts, then charcoal contains fixed air, whoſe weight may be increaſed to the double by the mere production of water, which deſtroys Mr. Lavoiſier's inferences.

The antiphlogiſtians explain the reduction of metallic calces with charcoal, by aſſuming that the charcoal does nothing more than attract the oxigenous principle from them by its ſuperior affinity; yet the acid of ſugar, which they allow to contain the inflammable principle, and contains no charcoal, and is even irreducible to charcoal, will alſo, I doubt not, reduce metallic calces, in a ſtrong heat.

To the arguments already adduced to prove that metallic calces are reduced by union with inflammable air, I ſhall add one more that appears to me unanſwerable. If to a ſolution of mercury in the Pruſſian acid, ſome filings of iron be added, and a ſmall quantity of vitriolic acid, this acid will immediately diſengage inflammable air from the iron, and this air uniting to the mercurial calx, will expel the Pruſſian acid and revive the mercury, as Mr. Scheele has diſcovered*. This experi-

* Scheele, p. 162, French tranſlation.

ment I repeated. Now let it be conſidered, that the Pruſſian acid does not contain dephlogiſticated air, but is a compound of fixed air, inflammable air, and volatile alkali, intimately combined together, and ſuffers no decompoſition or alteration by being expelled from the mercury, therefore the inflammable air does not affect it, but barely expels it by its ſuperior affinity to the mercurial calx, which at the ſame time it reduces.

REMARKS

REMARKS

OF

Mr. DE FOURCROY,

UPON THE

Calcination of Metals, the Metallic Calces or Oxides, the Formation of the Carbonic Acid, the Decompoſition of Water, &c.

THE words Calcination of Metals and Metallic Calces, have been adopted in conſequence of inaccurate obſervations, and refer only to ancient errors. The action of fire and air upon the metals, has been falſely compared to that of fire upon the calcareous ſtones, and the earthy reſidues of theſe burned metals to the earthy lime, or calx. Theſe errors have been long perceived, but no advantage has been derived from thence, in the perfection of chemical nomenclature. We have attempted to do this, by changing the expreſſion of Metallic Calces into that of Metallic Oxides, and, conſequently, the word Calcination of Metals, into that of Oxidation of Metals.

Theſe

Theſe new expreſſions denote, according to the ſpirit in which we have made the nomenclature, a combination of the metals with the baſe of vital air or oxigene; and we think it is demonſtrated, that the pretended calcination of metals is really nothing elſe but a combuſtion or union with oxigene; for, notwithſtanding what Mr. Kirwan ſays, theſe two expreſſions are really ſynonimous. The aſſertion which we preſent, is proved by the following facts. 1. Among elaſtic fluids, there is only vital air, which can calcine metals. 2. They are not calcined by atmoſpheric air, but in proportion to the quantity of vital air it contains. 3. In proportion as they burn, they abſorb, fix, and condenſe this vital air; which proves that the latter abandons the matter which held it fuſed or divided in the ſtate of an elaſtic fluid. 4. It is therefore only the ſolid part of vital air, or oxigene, which unites to metals. 5. It is for the ſame reaſon that this combuſtion is accompanied with heat and light, when it is rapid. 6. But as the caloric and light are bodies of ſuch levity, that we cannot appreciate their weight by our inſtruments, the loſs and diſengagement of theſe principles make no change in the weights in our experiments. 7. Metals therefore increaſe in weight, by the quantity of vital air they fix during their combuſtion. 8. All the ſemi metals, and imperfect metals, preſenting abſolutely the ſame phenomena

when

when they are heated with contact of air, there is no reaſon to believe that the calcination differs in any of them; their analogy, and that of the effects which are obſerved, prove, on the contrary, that one and the ſame phenomenon obtains in them all. 9. In all the various proceſſes by which metals are calcined, otherwiſe than by means of the air, they undergo abſolutely the ſame modification; their weight increaſes, and they loſe the metallic ſtate, in the ſame manner as by the ſimultaneous action of heat and the air.

All theſe poſitive and ſimple facts lead us to this reſult. The calcination of metal is, in every poſſible caſe, whether by air, water, acids, &c. a combination with oxigene, or a true oxidation.

By conſidering the various metallic oxides, we find, 1. That they differ in the ſeveral quantities of oxigene they require for their ſaturation. 2. That ſome loſe this oxigene by the ſimple contact of heat and light, ſometimes even by the action of the latter only, aſſiſted by very little heat. 3. That the greater number do not admit of the oxigene being driven off by theſe agents. 4. That no induction can be made, contrary to our doctrine, from this difference between the metallic oxides; becauſe, if ſo, it might be objected, with equal propriety, that becauſe the ſulphuric acid is ſeparated from certain metallic neutral ſalts, by the action of fire, and not from

from alkaline ſulfates, it exiſts in the former, but not in the latter; for the reaſoning would be equally perfect in both caſes. 5. That not only the oxigene is abſorbed in different doſes, by the various metallic ſubſtances, but that it is likewiſe combined in them after privation of a greater or leſs quantity of caloric and light; and that this doſe cauſes a variation both in the fixity of the oxigene, and the facility with which it may be diſengaged. This obſervation muſt agree with the weight and ſpecific heat of metallic oxides. 6. That each metallic oxide may exiſt in different ſtates of oxidation, from the ſmalleſt quantity poſſible, unto that which is neceſſary for its ſaturation; ſo that the oxidation of each metal ſtops, as it were, at different degrees. Thus it is that lead becomes oxidated, firſt of a grey and then of a yellow and red colour; and iron is black and brown. 7. That the periods of oxidation in each metal depend on circumſtances which are more or leſs favourable to the attraction of the metals with oxigene; the principal of which circumſtances is, a certain temperature neither too high nor too low. Thus a certain metal will abſorb, and fix only a very ſmall quantity of atmoſpheric oxigene, and never becomes any thing but an oxide of a certain nature, at the uſual temperature, whereas it will fix a much greater quantity, and its oxidation will become complete, if it

be

be ſtrongly heated; ſuch are zinc, iron, &c. 8. That the 17 known metallic ſubſtances, arſenic, tungſten, molybdena, cobalt, biſmuth, nickel, manganeſe, antimony, zinc, mercury, tin, lead, iron, copper, ſilver, gold, and platina, have different degrees of chemical attraction for the oxigene; part of which attractions are already known, and have been exhibited by Mr. Lavoiſier: thus manganeſe, zinc, iron, copper, mercury, ſilver, gold, follow each other immediately, from the ſtrongeſt to the weakeſt affinity for that body. 9. Laſtly, that the metallic oxides are not decompoſed or reduced into metals, but by the laws of attraction, followed by the oxigene: thus heat ſeparates it from ſome; one metal takes it from another; hydrogene, or inflammable gas, takes it from moſt metals; and carbone perhaps from all.

Such are the ſimple and few general principles which conſtitute our doctrine. We will venture to affirm, that they are founded on all the moſt poſitive facts of chemiſtry, which are the beſt known and underſtood; and that they are nothing more than the pure and ſimple reſult of all the united experiments upon the oxidation of metals: they are applicable to all the metals, and none of them require either a reverſement of theſe principles, or a particular theory. I thought it proper to preſent a ſketch of this doctrine here, in order that the chemiſts, and Mr. Kirwan in particular, might

might know the whole of the facts on which it is founded. I ſhall now proceed to examine the theory of Mr. Kirwan, and reply to the objections he has made.

This chemiſt thinks, like Stahl, that metals loſe their phlogiſton by calcination; and he takes this phlogiſton to be concrete inflammable gas. He admits therefore, in thoſe bodies, that which we call hydrogene. In proportion as metals are heated, their hydrogene combines, according to him, with the air which is precipitated; this combination forms fixed air, or the carbonic acid, which is fixed in ſuch a manner that metallic calces are compounds of metallic baſes with the fixed air. Mr. Kirwan thinks that ſeveral metals unite to water in their calcination, or to other ſubſtances which calcine them. Here therefore in this theory are at leaſt three different kinds of metallic calces; and this complication of theory is not ſupported by any proof, which to me appears ſufficient, as I think I ſhall be able to ſhew. The reduction of metallic calces is not better founded; it is, according to the author, either the decompoſition of fixed air, the tranſpoſition of its phlogiſton upon the baſe of the metal, and the ſeparation of the vital air for thoſe calces which are reduced by heat alone; or the diſengagement of fixed air produced by the addition of phlogiſton in ſuch calces as are not reduced but by the interpoſition of charcoal, oil, &c. or, laſtly (for he is obliged, notwithſtanding

ſtanding his repugnance, to admit the poſſibility in ſome caſes) the decompoſition of the water fixed in ſome calces. After having denied this decompoſition through the whole courſe of his work, he ends at laſt by avowing, that it is abſolutely poſſible, that at a very great degree of heat the water contained, according to him, in the calces of iron, may be decompoſed in their reduction. As the author had admitted three general ſpecies of calcination, it was neceſſary that he ſhould likewiſe admit three kinds of reduction. But how far does this complication of effects, ariſing from ſimilar cauſes, appear to me to be from the ſimplicity of nature. I cannot even forbear obſerving, that this diverſity of opinions reſpecting the ſame natural phenomenon, ſeems to have influenced the arrangement of Mr. Kirwan's ideas in this ſection of his work: the facts upon which the author relies, are not diſpoſed with ſufficient method to be eaſily conceived as a whole; and I have been obliged to read the ſection throughout a great number of times, and to meditate a long time to find a connection and relation between its ſeveral parts, which might be ſufficient to guide me, and to render me well acquainted with the thoughts of the author. I ſhall not therefore examine the facts in ſucceſſion, in the order of the diſſertation; but I ſhall diſcuſs them by bringing facts of the ſame kind together,

together, whatever place they may occupy in this ſection of the work.

Mr. Kirwan begins by referring to the proofs he has given in the Philoſophical Tranſactions for 1782, of the exiſtence of phlogiſton. He means to ſpeak of the inflammable gas diſengaged during the ſolution of moſt of the metals, and their precipitation in the metallic ſtate by other metals, without the diſengagement of inflammable gas in this laſt caſe. Mr. Lavoiſier has proved, in the Memoirs of 1782, that this laſt phenomenon is due to the tranſition of the oxigene of the diſſolved metal into that which takes its place, and conſequently relates to the affinities of that principle; with regard to the firſt circumſtance, it manifeſtly depends upon the decompoſition of water. Mr. Kirwan does not conceive why iron ſhould decompoſe the water, rather than the ſulphuric acid; or why the diſengaged hydrogene of the water did not deprive the ſulphur of its oxigene. Theſe phenomena appeared to him to be contrary to the theory we have eſtabliſhed; but he does not recollect that the affinity which obtains between two bodies ſingly, is ſubject to remarkable variation by the addition of a third. Thus iron and hydrogene decompoſe the ſulphuric acid when they act ſingly upon it at a high temperature; but when the iron and acid are in contact with water, the order of the affini-

ties

ties is immediately changed; the affinity of the iron for the oxigene of the water becomes ſtronger than that of the metal for the oxigene of the ſulphuric acid, becauſe the latter has a very conſiderable affinity for the water to which it adheres, and for the oxide of iron to which it tends to unite. Theſe two laſt mentioned affinities cauſe the acid to remain entire, and likewiſe afford the reaſon why the hydrogene of the water does not decompoſe the ſulphuric acid at the temperature of the ſolutions. Moreover, if this modification of the affinities were not ſufficient to explain the phenomenon in queſtion, Mr. Kirwan's objection might be anſwered by ſhewing, 1. That the acid is not decompoſed, becauſe it is found entire. 2. That the water is decompoſed, becauſe the metal cannot be oxided without the preſence of oxigene, which it takes from the water; and becauſe this oxigene cannot be ſeparated from the water without the hydrogene, or other principle of this fluid becoming diſengaged under the form of an elaſtic fluid by the help of caloric, which is diſengaged at the ſame time. 3. That the metal cannot afford inflammable gas, becauſe it does not contain it.

It is upon this laſt fact that we ought to inſiſt moſt ſtrongly, becauſe it is upon this that we differ moſt eſſentially with Mr. Kirwan. This philoſopher thinks that metals owe their metallic ſtate to the concreſcible part

of this gas or hydrogene, which he conſiders as phlogiſton, and that they are compounds of this principle with baſes or peculiar earths. We apprehend, on the contrary, that there is no proof that metallic ſubſtances contain hydrogene, but that their compoſition is unknown, becauſe their principles cannot be ſeparated, and becauſe they do nothing more than combine with various other natural bodies, inſtead of being decompoſed in all the changes they are made to undergo. In a word, every thing leads us to conclude, in our doctrine, that metals are, with reſpect to the ſtate of our knowledge, ſimple ſubſtances, whoſe various attractions require to be ſtudied. If we ſucceed in proving this aſſertion, all thoſe which conſtitute our theory will be proved, and conſequently the foundation upon which Mr. Kirwan has built his ſyſtem muſt give way. The accurate diſcuſſion of a ſingle fact may determine this queſtion; Is there one ſingle experiment which demonſtrates the preſence of ſolid inflammable gas, phlogiſton, or hydrogene, in the metals? If the ſupporters of phlogiſton can offer a ſingle fact of this nature, their theory is ſhaken only in part; but all that they have done, for ſeveral years paſt, has not decided the queſtion in their favour, and may, on the contrary, ſerve to confirm our doctrine. The collection of experiments and obſervations made by Mr. Kirwan on this head, in the ſection to which we ſubjoin the preſent Remarks, is

abſolutely

abſolutely of this kind. The diſtillation of an amalgam of zinc, conſiſting of ſeveral pounds of mercury, and 360 grains of zinc, which afforded ſome cubic inches of inflammable gas, cannot certainly be taken for a proof of the preſence of hydrogene or phlogiſton in that metal. For, 1. As Mr. Kirwan does not ſuppoſe that water exiſted in this amalgam, what can be the cauſe of this diſengagement in cloſed veſſels, and how does he himſelf explain the fact? 2. Can he depend upon ſuch ſlight circumſtances to admit the exiſtence of phlogiſton? 3. Several cubic inches of inflammable gas require no more than 3 or 4 grains of water; and how great is the difficulty to dry, in ſo complete a manner, ſome pounds of mercury ſo as to deprive it of the laſt particles of water which adhere ſo ſtrongly to this liquid metal? The Engliſh philoſopher himſelf admits, both in his work and his private letters, that it is very difficult to deprive mercury of all moiſture. The experiments of Dom Caſſebois, upon the curvature of mercury in the tubes of the barometer, prove that a few grains of water, introduced into a cylinder of this metal, mix with it, and adhere ſo intimately, that it diſappears, and its preſence may be certainly known by the convexity which the ſurface of the column of mercury immediately aſſumes, for it is plane only when perfectly dry. We find therefore, in the experiments on the amal-

gam, a fact entirely in our favour; for a few grains of water in the mercury will ſuffice to oxide a ſmall portion of the zinc, and produce the ſmall quantity of hydrogenous gas which is obtained. 5. A ſtrong proof of this truth is, that by a ſlight augmentation of the proportion of water, the production of hydrogenous gas is augmented in an accurate proportion. 6. The ſmall quantity of carbonic acid or fixed air which is found in the gas, diſengaged from this amalgam, likewiſe confirms our doctrine, for it cannot ariſe but from the carbure of iron, (plumbago) which is now admitted to exiſt in zinc, and conſtitutes the black powder, ſeparated from this metal in its diſſolutions; a ſubſtance which afforded great embarraſſment to chymiſts, before the new diſcoveries of carbone, or pure charcoal, in ſome of the metals.

As the decompoſition of water by iron is one of the principal foundations of our theory, Mr. Kirwan endeavours to attack it by reaſoning; for experiment can no more aſſiſt him than us in this queſtion. He thinks that when water in the vaporous form paſſes through a tube of red hot iron, in the experiment of Mr. Lavoiſier, it does nothing more than diſengage the inflammable gas of the iron, and combine with the metal. But Mr. Kirwan has not taken notice that this explanation cannot in any manner be reconciled with the facts, becauſe, 1. The augmentation of weight gained

gained by the iron when added to the weight of the inflammable gas contained, anſwers exactly to the quantity of water which has diſappeared. 2. By combining this hydrogenous gas with vital air, it is found that it abſorbs in burning a weight of the latter equal to that which the iron had acquired, and that it forms a quantity of water, equal to that which was employed in the oxidation of the iron.

Mr. Kirwan objects, that the oxigene of the water is fixed in that fluid, and does not contain much heat; but though the oxigene be more condenſed in water than in vital air, it nevertheleſs contains a conſiderable quantity of caloric, becauſe much heat is diſengaged from water in a number of caſes. It is therefore principally from the liquid oxigene of the water that the heat is diſengaged when iron is moiſtened, becauſe the metal which is by that means converted into the black oxide, contains after its oxidation the oxigene in a more condenſed and ſolid ſtate than when it compoſed part of the liquid.

A ſecond objection of Mr. Kirwan relates to the difference between this calx of iron made by water, and that which is formed by the abſorption of air. The ruſt of iron, ſays he, affords carbonic acid and vital air; the black teſſular iron formed by water affords no kind of air. This objection turns in reality to the advantage of the new doctrine. For the

black oxide of iron, or kind of ſolid ethiops into which water converts iron, is not ſaturated with all the oxigene the metal is capable of abſorbing. The metal adheres ſtrongly to the portion of oxigene which it contains; heat cannot diſengage it; it has a ſtronger tendency to abſorb more oxigene than facility of giving it out. It does not afford carbonic acid, becauſe it contains none.

Mr. Kirwan likewiſe oppoſes to us a beautiful experiment of Mr. Prieſtley, which it will not be difficult to apply with advantage to our doctrine. Mr. Prieſtley heated, with a burning glaſs, a ſmall piece of iron, in vital air obtained from precipitate per ſe; the air was diminiſhed and was abſorbed by the iron, which changed into ſcoriæ, and increaſed in weight in proportion to the quantity of air abſorbed: having afterwards heated this ſcoriæ in inflammable gas, water was formed, and the iron reſumed its metallic ſtate. We ſhall firſt obſerve that the expreſſion of the weights indicated by Mr. Kirwan is not perfectly exact, becauſe he always uſes the word nearly. 1. It is evident that the iron muſt have increaſed, very accurately proportional to the quantity of vital air fixed in its oxidation. 2. The hydrogenous gas abſorbed a part of this oxigene, with which it formed the water obtained by Mr. Prieſtley. 3. The iron did not recover its perfect metallic ſtate, nor reſume its original weight. But how, ſays Mr. Kirwan,

could the inflammable gas reduce the iron, or deprive it of oxigene, when, on the contrary, according to Mr. Lavoiſier's table of affinities, iron has a ſtronger affinity with oxigene than the baſe of inflammable gas has, and becauſe it is by virtue of this greater affinity that it decompoſes water. If this, which at firſt appears to be a very ſtrong objection, ſhould, when attentively examined, become a new proof in confirmation of the doctrine we ſupport, it will not, I think, be poſſible to deny all the advantages of this doctrine over thoſe which preceded it. Now the queſtion before us is exactly in this ſituation, as I ſhall proceed to ſhew.

It is very true that iron decompoſes water by virtue of its affinity for oxigene, which is greater than that which unites it to hydrogene; but it is not leſs true that this affinity has a limit: in fact, iron in contact with water itſelf, at the higheſt temperature, is never oxided further than to become black; it does not deprive the liquid of more oxigene than is required to convert it into ſpecular iron ore, which is black, brilliant, brittle, fuſible, cryſtallizable, or martial ethiops when it is reduced to powder. As long as this oxide is in contact with water only, and has no communication either with air or acids, or other metallic oxides, it remains conſtantly in this ſtate; and it is known that it is not ſaturated with oxigene, becauſe it then contains no more than

between 28 and 30 pounds *per* quintal, whereas by other proceſſes it can abſorb a much greater quantity. It is this point of oxidation of iron by water, which we call the limit of the affinity of this metal for oxigene, with relation to the adherence of the latter to hydrogene. Now iron takes oxigene from hydrogene only to this degree, and then its force of affinity for oxigene yields to that which keeps the hydrogene and oxigene united, and the iron no longer decompoſes the water; hence it is that when the internal part of the gun barrel through which water has been paſſed, is converted to a certain thickneſs into black oxide, the water ſuffers no further alteration; for this reaſon likewiſe it is that in the preparation of the martial ethiops of Lemery, if care be taken to keep the iron and the water from the contact of air, the metal remains in the form of a black powder at the bottom of the fluid; it is for this reaſon, laſtly, that this black oxide or martial ethiops is diſſolved in the ſulphuric and muriatic acids, almoſt without effervescence, and without affording hydrogenous gas. It will be no leſs eaſy from this primitive explanation, to ſay why hydrogenous gas reduces or revivifies the oxides of iron, by remarking that this reduction takes place only in thoſe oxides which are more advanced in their oxidation than the black iron or ethiops, and that it ſtops at the moment when the oxides of iron are brought to the ſtate of ethiops. In this manner

manner it is that the brown, red, yellow, and white oxides of iron, abſorb hydrogenous gas, become of a deeper colour, and are converted into a black powder, which is attracted by the magnet, but is not pure iron, but that which we call the black oxide of this metal. The hydrogene does not take from the oxides of iron any greater quantity of oxigene than that which they contained beyond their oxidation to the black colour, becauſe this quantity has a greater affinity with the hydrogene than with the iron; but when the reduction is arrived to this point, it proceeds no further; the laſt portion of oxigene which the iron contains, adheres more ſtrongly to it than it tends to unite with the hydrogene; there is no other known ſubſtance but manganeſe, zinc, and carbone, which can deprive iron of this laſt portion of oxigene, and even for this purpoſe there is required a very elevated temperature, as the art of founding and refining of iron evinces. In the experiment of Dr. Prieſtley, the iron was oxided by the vital air, beyond the ſtate of black oxide, and the volume of gas abſorbed muſt have produced a great diminution, as it is known that to ſaturate the oxigenous principle there is required near one ſixth part by weight of the hydrogenous gas, which is only one fourteenth of the ſpecific weight of vital air. Hence we think, as the expreſſions uſed by Mr. Prieſtley authorize us, that after the reduction of this ſcoria of iron, there muſt have

have been a ſmall exceſs of weight, beyond what was taken to be calcined in vital air. This exceſs of weight after the reduction, anſwers to the quantity of oxigene neceſſary to keep the iron in the ſtate of black oxide or ethiops. If an additional proof be required of the theory of the affinities of the metals with oxigene, comparatively with that of hydrogene for the ſame oxidant or acidifiant principle, we may here mention the remarkable fact, that the oxides of lead and biſmuth ſtrongly abſorb the hydrogene of inflammable gas, and are completely reduced, becauſe they are not ſuſceptible of decompoſing water when alone; whereas zinc, which poſſeſſes this laſt property in a moſt eminent degree, affords an oxide whoſe whiteneſs is in no manner altered, and which is not at all reduced by the contact of hydrogenous gas. It is for this reaſon that the white oxide of zinc ought to be preferred, as a pigment, to that of lead, of which likewiſe it does not poſſeſs the dangerous qualities, as Mr. De Morveau has propoſed.

I hope therefore that I have eſtabliſhed, on grounds of ſufficient ſolidity, that the partial reduction of an oxide of iron by hydrogenous gas is not contrary to the affinities which effect the decompoſition of water. The objection of Mr. Kirwan which follows, and is founded on the decompoſition of water by charcoal, poſſeſſes no more real value than the preceding.

Mr.

Mr. Kirwan ſpecifies the circumſtances in which the metallic oxides contain carbonic acid, and thoſe in which they contain water. Such as are formed in a low heat without ignition, are, according to him, in the firſt caſe; and thoſe which are prepared at an elevated temperature, are in the ſecond. But beſides what we have already obſerved, at the commencement of theſe remarks, againſt this double ſtate of metallic oxides, which moreover is not proved by any direct experiment, there is an inſurmountable difficulty in this opinion; namely, that Mr. Kirwan has never converted hydrogenous or inflammable gas into carbonic acid or into water, according to the different temperatures employed in their combuſtion. In whatever manner the combination between theſe two bodies is brought about, the reſult is always water: if in almoſt every caſe a ſmall quantity of carbonic acid is obtained from this combuſtion, it is inconſiderable, and always relative to the carbone contained in the gas, and ariſing from the iron or the zinc, which ſerved to extract the hydrogene from the water. Moreover, it is known with what facility the hydrogenous gas diſſolves charcoal; the great condenſation it experiences, and the ſpecific gravity it acquires. Laſtly, this diſſolution of carbone in hydrogenous gas, which is ſo frequent, that this gas has never yet been obtained in a ſtate of perfect purity, ſeems to be the cauſe of the ſtrong and fœtid ſmell, which every one knows

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it to poſſeſs. Nothing therefore proves that the carbonic acid, or fixed air, is formed by the combination of vital air, or oxigene, with the baſe of inflammable air, or hydrogene; all the facts, on the contrary, do not permit us to doubt but that this combination never affords any product but water; and it is an hypotheſis abſolutely void of proof to admit, after this, the formation of the carbonic acid, and its union in the oxidation of metals. If minium, and the oxides of lead in general, afford this acid by the action of fire, it is becauſe they have abſorbed it by the contact of air, as is proved by the quantity of this acid, which is greater the longer the oxides have been expoſed to the atmoſphere; this happens likewiſe to the oxides of iron, and to precipitate per ſe, or the red oxide of mercury, made by the air. This laſt changes its colour, and becomes brown in proportion as it abſorbs the carbonic acid, as Mr. le Blanc has proved in a Memoir read to the Academy.

Mr. Kirwan, to prove the difference which he admits between theſe two claſſes of oxides or metallic calces, obſerves, that the muriatic acid diſtilled from minium, and precipitate per ſe, in which he admits fixed air, becomes dephlogiſticated by abſorbing this fixed air; and that it is not changed by diſtillation from the calces of zinc, antimony, and iron. But Mr. Berthollet has proved that the oxigenated muriatic acid does not contain fixed air, and that

that it is merely as the name we have given to it expreſſes a combination of muriatic acid and oxigene; we do not therefore perceive any other difference between the metallic oxides which oxigenate this acid, and thoſe which do not produce the ſame alteration in it, except the various adherence of the oxigene, and the different degrees of affinity exiſting between this principle and the metals. It is a rule which appears to be general, that thoſe metals to which the oxigene does not adhere ſtrongly, and from which it can be ſeparated, either wholly or in part, by light and heat, and by moſt other metallic ſubſtances, eaſily yield this principle to the muriatic acid, while the metals which ſtrongly retain the oxigene do not give it out to this acid.

Mr. Kirwan is not more happy in the other facts which he has collected to prove that the metallic oxides made by a gentle heat contain only fixed air. The carbonic acid which Mr. Hermſtad obtained from the oxide of manganeſe diſtilled with iron, is produced only from that which the oxide abſorbed from the atmoſphere, or from the charcoal contained in the iron, which burns by means of the oxigene diſengaged from the manganeſe. If red precipitate, thus treated with iron, ſometimes affords various doſes of this acid, and ſometimes affords none at all, this depends on the ſtate of the oxide of the mercury, which is more or leſs oxided, or has been either recently made

or long expoſed to the air, whether it contains nitrous acid, or is entirely deprived of it, and, laſtly, upon the nature of the iron, which retains more or leſs charcoal. The ſame obſervations upon the ſtate of red precipitate explain why this oxide heated with biſmuth afforded carbonic acid, which it contained. If Mr. Kirwan will maturely reflect upon the experiments he has made, he will ſoon perceive that moſt of them are entirely to the advantage of our doctrine. Red precipitate and lead heated together afforded no air, becauſe the lead only abſorbed the oxigene of the mercury. When zinc and tin became inflamed in their diſtillation with the ſame mercurial oxide, and did not afford elaſtic fluid, is it not clear, 1. That theſe two metals did nothing more than deprive the mercury of its oxigene? 2. That, by combining with this principle, they condenſed it, and ſeparated more caloric and light than the latter metal, and that this is the reaſon why they were inflamed. The copper did nothing more than abſorb the oxigene of the mercury, and revive that metal? Lead agitated with water, and in a certain volume of atmoſpheric air, afforded Mr. Kirwan a ſomewhat conſiderable quantity of carbonic acid; but to conclude that the water united to the phlogiſton of the metal to form this acid, is advancing an hypotheſis which in no wiſe agrees with the experiments; it is much more probable that this carbonic acid proceeded

ceeded from the water or the air, and perhaps from carbone contained in the lead; for though it has not yet been found in this metal, it is not impoſſible but that, during its fuſion in the midſt of coals, it may have abſorbed part of their combuſtible matter *.

The facility and promptitude with which the metals become oxided when they are divided by mercury, is now no longer a problem; but if the oxides of zinc and lead, prepared by agitating an amalgam in water, have afforded car-

* Since theſe remarks of Mr. de Fourcroy were written, I have carefully repeated the experiment of the oxidation of lead by the intermedium of water, as deſcribed by Mr. Kirwan. The only difference which deſerves to be noticed in the proceſs I followed, is, that inſtead of evaporating in the open air, the water which had been neceſſary to diſengage the lead out of the bottle in which it had been cloſed, I diſtilled it in a ſmall retort, from which the elaſtic vapours of courſe expelled all the air. The lead, which was for the moſt part reduced into an oxide, did not become blue, as in the experiment of Mr. Kirwan, but it aſſumed a reddiſh caſt, and it gave out no gas. I have repeated the ſame experiment upon litharge, which had been newly prepared, and it likewiſe afforded no gas.

My experiments entirely agree with thoſe of Mr. Gren, who did not obtain gas by ſubjecting an oxide of lead, which he had himſelf prepared, to a ſtrong heat. (Beytrage zu der chemiſcen, annalen. 1787.)

Mr. Gren deſcribes a great number of experiments, whoſe reſults are contrary to thoſe of Mr. Kirwan. I ſhall content myſelf with tranſlating the following paſſage, which refers to the principal of them. "My eſſays evidently prove that fixed air is not produced either by the combuſtion of phoſphorus, or of ſulphur, or of metallic inflammable gas, by the decompoſition of common air and nitrous gas, by the calcination of metals, or by the amalgamation of lead."

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bonic acid, it aroſe, no doubt, from the cauſes already mentioned.

By inſiſting upon all theſe experiments, Mr. Kirwan is deſirous not only of proving that the metallic oxides contain either water or carbonic acid, but it is likewiſe his intention to demonſtrate, that this acid is compoſed of oxigene and hydrogene, that is to ſay, of dephlogiſticated air, and the baſe of inflammable gas, which we know he ſubſtitutes inſtead of the phlogiſton of Stahl. He firſt inſiſts upon an experiment of Mr. Hermſtadt, who having deprived the oxide of manganeſe of the vital air it afforded, by a ſtrong heat afterwards ignited this oxide in an earthen tube, and paſſed the carbonic acid over it eight ſucceſſive times. This air, ſays he, became ſo pure, that it was capable of maintaining combuſtion; but as he has not, in relating this experiment, given any account of the quality of this air as determined by the eudiometer, nor any indication of its quantity, we can perceive no other fact than the abſorption of the carbonic acid by the manganeſe or by the water through which it paſſed, and the diſengagement of a new quantity of vital air from this ſemi metal, which might perhaps be even the air uſually contained in the water, and expelled by the carbonic acid which occupied its place.

With regard to the alteration of this acid by the electric ſpark which was obſerved and deſcribed by Mr. Monge, and from which

Mr.

Mr. Kirwan deduces an inference in favour of his theory, our aſſociate has himſelf explained the fact.

All the experiments which relate to the formation of the carbonic acid, prove the exiſtence of carbone in all caſes where that acid was formed. The oxidation of metals does not produce it, unleſs they contain carbone of iron, or plumbago, as iron and zinc do. Carbone is certainly diſengaged in vapours from the lungs, and this ought not to ſurprize thoſe philoſophers, who at preſent are aware that this body which is ſo fixed when dry and alone, is completely and eaſily diſſolved in ſeveral elaſtic fluids, ſuch as vital air, hydrogenous gas, and even the azotic gas of animal ſubſtances, as I have found in my reſearches upon theſe gaſes.

One of the experiments upon which Mr. Kirwan grounds his opinion of the nature of fixed air, or carbonic acid, which he conſiders as a compound of hydrogene or phlogiſton, and oxigene or vital air, and which differs from water, according to him, only in its containing a larger quantity of hydrogene; is that of Mr. Prieſtley, in which that philoſopher, by paſſing air over charcoal in a red-hot earthen tube, obtained much inflammable air together with fixed air; and by burning this inflammable air with an equal volume of dephlogiſticated air, he obtained a greater quantity of fixed air than that of the inflammable

air made uſe of; but this reſult is not favourable to him, for how, according to his theory, can the air change charcoal into inflammable air? It is much better proved that the inflammable gas, and the carbonic acid obtained, ariſe from the decompoſition of the water diſſolved in this air, and that this inflammable gas, holding much carbone in ſolution, afforded a large quantity of carbonic acid, and a ſmall quantity of water in its combuſtion with vital air. Beſides, we muſt not forget, 1. That no one has changed all the charcoal into inflammable gas, which is neceſſary, according to Mr. Kirwan's theory. 2. That pure inflammable gas, or hydrogene, affords only pure water in its combination with oxigene. 3. That it is abſolutely neceſſary that charcoal ſhould be preſent in the formation of carbonic acid or fixed air. 4. That when hydrogenous gas, which holds much carbone in ſolution, is burned, ſuch as was that diſengaged in the experiment of Mr. Prieſtley, a much greater quantity of vital air is neceſſary, than to burn an equal volume of pure hydrogenous gas, and that by this combuſtion a mixture of water and carbonic acid is obtained proportional to the quantities of hydrogene and carbone which form it. Theſe poſitive facts abſolutely deſtroy the theory of Mr. Kirwan, and agree perfectly with our doctrine.

It is difficult to conceive how Mr. Kirwan thinks to invalidate our doctrine of the reduction of metallic oxides by carbone, by

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virtue of the ſtrong affinity of the latter for oxigene, by ſuppoſing that the oxalic acid, or acid of ſugar, ſhould reduce the oxides by a ſtrong heat, though, ſays he, this acid does not contain charcoal, and cannot be reduced to charcoal. But we reply, 1. That he has not effected this reduction. 2. That ſuppoſing it to exiſt, and to be proved, it would ariſe either from the hydrogene, which really exiſts in this acid, and takes the oxigene from the oxides, or to the carbone which this acid very aſſuredly contains, ſince, during its decompoſition by heat, the carbonic acid is obtained by the ſimple union of oxigene and carbone, and the hydrogenous gas which holds carbone in ſolution. We have ſhewn, in the remark annexed to the preceding ſection, that the oxalic acid is a combination of hydrogene, carbone, and oxigene, in proportions yet undetermined, that it differs from the other vegetable acids only in theſe proportions, and that if the relative quantities of the principles be varied by any circumſtance, the combination of this acid is quickly altered.

SECT. X.

Of the Diſſolution of Metals.

THE general opinion of chymiſts, ſince the beginning of this century, has always been, that the ſolution of metals proceeds from their affinity to the menſtruums that diſſolve them; yet, as they have alſo a ſtrong affinity to phlogiſton, and muſt be deprived of part of it before they can be diſſolved, I found it neceſſary to explain this matter more circumſtantially in a paper contained in the Philoſophical Tranſactions of the year 1784; but being at that time unacquainted with the conſtitution of the mineral acids (a more intimate acquaintance with which I acknowledge to have derived from attention to the writings of Mr. Lavoiſier, and Berthollet) I neglected mentioning, that the nitrous acid is always partially decompoſed in the act of diſſolving metals; that its fixed air and part of the undecompoſed acid unites to the metal, while another part of the decompoſed acid, namely, its baſis, uniting with the phlogiſton of the metal, forms nitrous air, part of which flies off and part is retained: the vitriolic acid, on the contrary, is ſometimes partially decom-

decompoſed, and ſometimes not, according to its proportion of water. If it be concentrated and heated, its fixed air, and part of its undecompoſed acid, will unite to the metallic body, while its baſis will unite to the phlogiſton of the metal, and form ſulphur; or it will only be partially decompoſed, its baſis retaining part of its fixed air, and partly uniting to the phlogiſton of the metal, and thus forming vitriolic air, which generally holds ſulphur in ſolution, part of this air will eſcape, and part will be retained. But if the vitriolic acid be dilute, it will not unite to the phlogiſton, nor conſequently be decompoſed, but will expel the phlogiſton in the form of inflammable air, and unite to the metal. The arſenical and phoſphoric acids are alſo capable of phlogiſtication, but not the marine acid, nor the vegetable acids, as far as I can recollect.

The antiphlogiſtians think that metals are ſoluble in acids, merely by their affinity to the oxigenous principle*, with which, during ſolution, they become ſaturated: conſequently all acids are decompoſed in diſſolving metals, or at leaſt promote the decompoſition of water, a ſuppoſition which I have already ſhewn to be deſtitute of foundation.

If metals become ſoluble by ſaturation with the oxigenous principle, I would aſk,

* Mem. Par. 1782, p. 492.

1ſt. Why calces, ſaturated with the oxigenous principle, are not ſoluble in water, nor even in vitriolic acid?

2dly. Why the calces of iron, tin, and regulus of antimony, ſaturated with the oxigenous principle, are inſoluble in the nitrous acid, whereas, when unſaturated, they are ſoluble in that acid? whereas the calces of lead, ſilver, and mercury, when ſaturated, are ſoluble in that acid. Do not theſe differences indicate another affinity beſides that of the oxigenous principle?

3dly. Why the calces of iron are more eaſily diſſolved by the marine than by the nitrous acid, even when unſaturated?

4thly. Why moſt calces are more eaſily ſolved by the vegetable acids, than their reſpective metals?

5thly. Why a ſolution of iron in dilute vitriolic acid is decompoſed by expoſure to the air? and why an exceſs of acid re-diſſolves the calx, or prevents its precipitation?

6thly. Why a ſolution of zinc in the dilute vitriolic acid is not ſo eaſily decompoſed by expoſure to the air?

7thly. Why a ſolution of iron in the marine acid is not eaſily decompoſed by expoſure to the air?

8thly. Why regulus of antimony totally decompoſes the nitrous acid, while copper, which has a greater affinity to the oxigenous principle, does not decompoſe it totally?

9thly.

9thly. How comes it to paſs, that calces of gold are ſoluble in the nitrous acid, and calces of iron inſoluble? Do not all theſe phænomena prove, that another affinity intervenes, beſides that of metals, to the oxigenous principle?

10thly. Whence do copper, lead, and zinc, diſſolved in cauſtic fixed alkali, and copper in cauſtic volatile alkali, derive the oxigenous principle?

11thly. Since zinc and iron are ſoluble in the concentrated vitriolic acid, only by the aſſiſtance of heat, and in the dilute acid, without heat, the antiphlogiſtians muſt ſay, that zinc and iron take away the oxigenous principle from ſulphur, only by the aſſiſtance of heat, but are able to take it from the inflammable principle without the aſſiſtance of heat; yet by their own doctrine, the oxigenous principle has a far greater affinity to the inflammable principle than to ſulphur. How is this conſiſtent?

REMARKS

UPON THE

TENTH SECTION,

CONCERNING THE

DISSOLUTION OF METALS.

BY

Mr. De FOURCROY.

THE tenth ſection, in which Mr. Kirwan treats of the ſolution of the metals in acids, is one of the ſhorteſt, becauſe the author has already ſpoken of this phenomenon in various parts of his work, and muſt unavoidably have entered into repetitions. The ſame reaſons oblige us to be much more conciſe in our remarks, than in many of the foregoing.

As Mr. Kirwan has not given an account of our doctrine on this head, which is ſufficiently ample and clear, we ſhall here exhibit the chief or fundamental principles relating to the diſſolution of metals in the acids.

1. The

1. The metals cannot unite with the acids, but after they have been oxided or combined with oxigene.

2. It is neceſſary that the metals ſhould contain determinate quantities of oxigene to combine with the acids; within this term of oxidation they do not unite but with difficulty; beyond it they are ſeparated with more or leſs facility.

3. This determinate degree of oxidation for the degrees of ſolubility, is not only different in the different metals in the ſame acid, but likewiſe for each metal in particular in the ſeveral acids. The degree of oxidation neceſſary in each metal to unite with each acid, is not yet known, except in certain caſes; but enough is known to juſtify our placing the aſſertion we have made among the chemical axioms.

4. In every metallic ſolution by an acid, the metal, in order to become oxided, decompoſes either the acid itſelf or the water of ſolution, or it obtains from the atmoſphere the requiſite quantity of oxigene. In the ſecond caſe, hydrogenous gas, in a ſtate of greater or leſs purity, is diſengaged, and the acid remains entire without decompoſition; which is proved by the quantity of alkali neceſſary to ſaturate it. In the firſt caſe, one of the principles of the acid, or the acid deprived of part of its oxigene, is diſengaged and fuſed in the caloric, which is ſeparated at the ſame time;

time; ſuch are nitrous gas and ſulphureous acid gas. In the third caſe, neither the water nor the acid are changed; ſuch is the ſolution of copper by the acetous acid.

5. The muriatic acid, and the vegetable acids which are formed of radicals or acidifiable principles, which have more affinity with oxigene than the metals have, are not decompoſed by theſe metals, and the oxigene is always afforded to theſe laſt by the water or the atmoſphere. Hence the ſolutions by theſe acids afford only hydrogenous gas, or do not effervesce at all.

6. Theſe laſt mentioned acids ſo greatly facilitate the decompoſition of water by the metals, or augment their affinity for oxigene ſo much, that ſuch of the metals as would not alone decompoſe that liquid, even at a very high temperature, are by this means rendered capable of effecting it, as is ſeen in tin, copper, &c.

There are ſome caſes in which the water and the acid are at the ſame time decompoſed by the metal, as in the ſolution of tin in the nitric acid, according to the obſervation of Mr. De Morveau. Tin is ſo greedy of oxigene, and requires ſo large a quantity for its ſaturation, that after having abſorbed that of the nitric acid, and reduced it to the ſtate of azote, it decompoſes likewiſe the water, and diſengages hydrogene. Theſe two principles being ſeparated from their firſt compounds, unite

 together,

together, and immediately form ammoniac. Hence there is no ſenſible diſengagement of elaſtic fluid. In this caſe it appears, that the formation of ammoniac, in the ſolution of tin by the nitric acid, always takes place; for by throwing quicklime, or cauſtic fixed alkali, into this ſolution, there is always a diſengagement of ammoniac.

9. It follows, from all that has hitherto been ſaid, that in every metallic ſolution in which the acid is decompoſed, two doſes of this ſalt are required, of which the mind conceives the neceſſity. 1. That whoſe decompoſition ſupplies the metal with oxigene. 2. That which diſſolves the oxided metal.

10. Hence if no greater quantity of acid be added to a metal than is neceſſary for its oxidation, it will be oxided, and not diſſolved. Thus it is that a few drops of concentrated nitric acid being thrown upon tin, antimony, biſmuth, and even zinc, quickly reduce the metals into white, dry, and pulverulent oxides.

11. From this accurate diſtinction of the two doſes of acid, we ſee why a metal, though very greedy of oxigene, does not decompoſe this acid ſufficiently, nor deprive it of enough of oxigene to ſaturate itſelf; for if too highly charged with this principle, it would not unite to the undecompoſed portion of the acid, and there would be no ſolution; but inſtead of ſaturating itſelf in this manner, in proportion as the metal arrives at the determinate

point

point of oxidation, the acid diſſolves it, and the metal does not decompoſe it beyond that point, becauſe its affinity with the acid is then ſtronger than with a greater doſe of the oxigenous principle.

12. Various circumſtances, and eſpecially an elevated temperature, change theſe attractions; they increaſe that of the metal for oxigene, and by favouring its ſaturation with that principle, they either prevent its uniting with the acid, or effect its ſeparation: the former event takes place in the mixtures of acids and metals, whoſe mutual action is increaſed by a ſtrong temperature, and the latter takes place in moſt metallic ſolutions, when they are too ſtrongly heated.

13. Moſt metallic ſolutions, which are left expoſed to the air, abſorb oxigene with more or leſs facility; and the metals which they contain becoming more oxided than before, ſeparate and fall down; ſo that there is not one of theſe ſolutions which remains in the ſame ſtate if expoſed to air, or which can be conſidered as abſolutely permanent.

14. Since the metals cannot remain united to the acids, but in the ſtate of oxides of a determinate degree, it is eaſily conceived, that by plunging into a metallic ſolution a metal which has a ſtronger affinity with oxigene than that which is diſſolved, the former muſt deprive the latter of its oxigene, take its place in the acid, and cauſe the ſecond to ſubſide in

a form more or leſs metallic, accordingly as it has deprived it of more or leſs oxigene. This is the reaſon of the precipitation of ſilver by copper, copper by iron, &c.

Let this ſimple theory, which is merely the reſult of the facts, be now compared with the complicated explanations which Mr. Kirwan gives of metallic ſolutions, and it will ſoon be evident which opinion approaches neareſt the truth. This compariſon, made with that reſerve and circumſpection which are neceſſary in objects of this nature, appears to me to be ſo much in favour of our doctrine, that there is ſcarcely any fact relating to metallic ſolutions, which cannot be eaſily and clearly explained by its means. To exhibit proofs, to which Mr. Kirwan himſelf cannot refuſe his aſſent, for he certainly has nothing at heart but the diſcovery of truth, I ſhall proceed to ſhew, 1. That moſt of the objections which he exhibits in the form of queſtions in this part of his work, may be removed by a more intimate knowledge of the principles here laid down*. 2. That thoſe which are not accounted for upon theſe principles, are matters of fact, which no theory can explain.

1. The oxides, which are ſaturated with oxigene, are more ſoluble in water than the

* The numbers which follow, correſpond with thoſe of the queſtions propoſed by Mr. Kirwan; theſe being ſuppoſed to be known, are no otherwiſe referred to in this place, than by the anſwers made to them.

metals

metals from whence they are obtained; ſuch are thoſe of arſenic, antimony, molybdena, and tungſten; the ſulphuric acid does not diſſolve them all: this is a fact which cannot be explained in any theory, becauſe it depends on the cauſe of the affinities, which will perhaps never be known, or which, at leaſt, we are very far from knowing at preſent; it is a ſimple obſerved fact, that the metallic oxides, which are moſt ſoluble in the ſulphuric acid, are gradually precipitated by expoſing the ſolutions to the air of the atmoſphere, from which they abſorb oxigene: it is for the ſame reaſon, and becauſe they have paſſed the point of oxidation neceſſary for them to remain united to the ſulphuric acid, that ſome oxides cannot be diſſolved.

2. The oxides of iron, tin, and antimony, when ſaturated with oxigene, are not ſoluble in the nitric acid by the ſame law obſerved for all the acids; this inſolubility does not exiſt with regard to thoſe of ſilver, mercury, and lead; this likewiſe is a fact which depends on the law of the attractions which we can only exhibit: nevertheleſs we may in this place obſerve that theſe laſt metals have much leſs attraction for the oxigene than the former, and that their tendency to combination not being equally ſatisfied, it is natural to deduce their ſolubility from this circumſtance. We may likewiſe obſerve, that Mr. Kirwan will not find an anſwer to theſe queſtions, more

more readily than to the following: Why have ſome acids more affinity with the alkalis than with calcareous earth? and why have other acids a ſtronger affinity with this laſt than with fixed alkalis?

3. The muriatic acid diſſolves the oxides of iron more eaſily than the nitric acid, probably by virtue of its extreme tendency to unite with an exceſs of oxigene.

4. The vegetable acids diſſolve this oxide more readily for the ſame reaſon; moſt of them tend to abſorb more oxigene than they contain; and for this reaſon ſeveral of them take oxigene from the nitric acid, and become by that means more ſtrongly acid than before.

5. A ſolution of iron in the ſulphuric acid being expoſed to the air, lets fall the oxide of iron, becauſe it abſorbs oxigene; this aſſertion is proved by accurate experiments: an exceſs of ſulphuric acid does not re-diſſolve this oxide for any other reaſon than becauſe the iron containing more oxigene, requires more acid to hold it in ſolution; but in proportion as this metal abſorbs an additional quantity of atmoſpheric oxigene, it becomes again inſoluble in the quantity of acid which was added, and requires a new portion to re-diſſolve it; theſe additions of ſulphuric acid, proportional to that of the atmoſpheric oxigene in the iron, will diſſolve it, until the oxidation is complete.

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6. A ſolution of zinc in the ſulphuric acid, diluted with water, is not precipitated by the contact of air, becauſe the oxide of zinc, however it may be loaded with oxigene, appears to be ſoluble in this acid.

7. The decompoſition of the muriate of iron by the air, is not ſo eaſy as that of the ſulphate, doubtleſs becauſe of the ſtrong attraction of the muriatic acid for oxigene: it is known that the moſt highly charged oxide of iron with oxigene is ſoluble in this acid.

8. Antimony totally decompoſes the nitric acid; and copper, though it has a ſtronger affinity with oxigene, does not decompoſe it in the ſame manner, becauſe the ſemi-metal requires much more oxigene than the other does to ſaturate it; hence the oxide of antimony does not remain long diſſolved in the nitric acid.

9. The oxide of gold is ſoluble in the nitric acid, though the oxide of iron is not, becauſe the firſt has much leſs affinity than the ſecond with oxigene, and contains much leſs; moreover, this is a ſimple fact, which is no more explicable in one theory than in another, and which conſequently neither advances the doctrine of Mr. Kirwan, nor weakens ours.

10. When zinc is diſſolved in the cauſtic fixed alkali, and in ammoniac, it is by virtue of the decompoſition of the water which theſe combinations produce; hence there is no ſolution without a diſengagement of hydrogenous gas,

gas, as Messrs. De Lassone and the Academicians of Dijon have shewn. Mr. Gengembre has proved, in his researches on the sulphurated and phosphorated hydrogenous gas, or hepatic and phosphoric airs, that sulphur which does not decompose water at a low temperature, becomes capable when it is assisted by an alkaline substance, and that this is the cause of the formation and disengagement of these gases which are merely, as their new names imply, solutions of sulphur and phosphorus in hydrogenous gas. I have confirmed, by many experiments, this ingenious theory in my researches on hepatic gas *.

The same thing happens to zinc which does not decompose water, except very slowly at a mean temperature; but an alkali favours this decomposition, the metal seizes the oxigene of the water, and disengages the hydrogene fused in the caloric, which is separated at the same time that the reaction takes place between the component parts of these substances. With respect to lead and copper dissolved in the liquid alkalies, as this solution is not accompanied with a disengagement of hydrogenous gas, it is more than probable that these metals absorb from the atmosphere the oxigene they require for their solution. We have already made this observation upon

* Memoirs of the Royal Academy of Sciences, for the year 1786, now in the press.

the ſolution of copper in the acid of vinegar. We may here add, that it is by virtue of this abſorption of the atmoſpheric oxigene by copper, in the caſes where this metal is diſſolved in vegetable acids, that copper veſſels do not become oxided in œconomical uſes until the fluids they contain are cold.

11. That zinc and iron are not ſoluble in the concentrated ſulphuric acid, but by the aſſiſtance of heat, though they are ſoluble in the cold, in the ſame acid diluted with water, is no ground for the inference that we deceive ourſelves in affirming from experience, that the oxigene has more affinity with hydrogene than with ſulphur; for this apparent difficulty which is experienced in ſeparating oxigene from ſulphur, by means of the metals, is really leſs than that which muſt be got over to decompoſe water by the ſame metals, as we ſhall proceed to ſhew. Mr. Kirwan has not ſufficiently weighed all the circumſtances of the facts upon which our doctrine is founded in this reſpect. 1. Iron does not ſtrongly and readily decompoſe water when theſe two bodies act alone upon each other, except at a temperature much more elevated than that which is neceſſary for the decompoſition of the ſulphuric acid by the ſame metal. 2. When iron, water, and ſulphuric acid are placed in contact, a greater number of affinities concur to produce changes in theſe bodies than in the two former caſes.

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In the latter experiment, the iron not only tends to unite with the oxigene of the water, but the ſulphuric acid likewiſe tends to combine with the oxide of the iron; this ſecond attraction increaſes, for the moment, that of the iron for the oxigene, and its effect is ſuch as renders the decompoſition of the water more eaſy and quick than it would have been with iron alone.

SECT. XI.

Of the Precipitation of Metals by each other.

TO explain the precipitation of metals diſſolved in acids, by other metals, Mr. Lavoiſier thinks it ſufficient that the oxigenous principle ſhould have a greater affinity to the *precipitant* than to the *precipitated* metal; thus, in his ſyſtem, copper precipitates mercury, becauſe copper has a greater affinity to the oxigenous principle, than mercury has to that principle*.

As to the proportion of the oxigenous principle neceſſary to the ſolution of different metals, he deduces it from the quantity of one metal neceſſary to the precipitation of a given quantity of another metal by this analogy: *As the quantity of the* PRECIPITANT *is to that of the* PRECIPITATED *metal, ſo is the quantity of the oxigenous principle neceſſary for the ſolution of the precipitated, to that neceſſary for the ſolution of the precipitant.* Thus, ſince 135 gr. of mercury are neceſſary for the precipitation of 100 gr. of ſilver from the nitrous acid, it is evi-

* Mem. Par. 1782, p. 512.

dent

dent that 135 gr. of mercury require for their ſolution the ſame quantity of the oxigenous principle as 100 gr. of ſilver, and therefore that the quantity neceſſary to diſſolve 100 gr. of mercury, is to that neceſſary for the ſolution of 100 gr. of ſilver, as 100 to 135. Now by his own experiments, 8 gr. of the oxigenous principle are neceſſary to diſſolve 100 gr. of mercury, therefore 10,8 are neceſſary for the ſolution of 100 gr. of ſilver. The proportion of the *precipitants* to the *precipitated*, he finds, in all caſes, by Mr. Bergman's experiments: his general formula may be expreſſed thus:

Let the weight of the precipitant be P, that of the precipitated p, that of the oxigenous principle neceſſary for the ſolution of the precipitant O, and that neceſſary for the ſolution of the precipitated o; then, as P. p : : o. O.

By theſe means he found the abſolute quantity of the oxigenous principle neceſſary for the ſolution by precipitation of 100 gr. of the different metals, to be as expreſſed in the ſecond column of the annexed table, and that neceſſary for ſolution only, as in the third column.

Metals.	Oxigenous principle. Gr.	For ſolution merely.
100 gr. of Platina	81,690	
Gold	43,612	
Iron	27 } 37 }	
Copper	36,000	15,85
Cobalt	29,190	
Manganeſe	21,176	
Zinc	19,637	
Nikel	14,721	
Reg. of ant.	13,746	22,383
Tin	14	23,555
Reg. of arſ.	11,739 / 24,743	
Silver	10,800	
Biſmuth	9,622	
Mercury	8,000	
Lead	4,470	14,190

But the phænomena of precipitation are much more complicated; I have already endeavoured to explain many of them on a former occaſion, of which I ſhall ſelect a few, and would wiſh to know how they may be explained on the principles of the new theory.

1ſt. A ſolution of gold in aqua regia is precipitable in its metallic form, by a freſh made ſolution of vitriol of iron; but not by a ſolution of vitriol of copper, or of any other metal. The antiphlogiſtians will probably reply,

ply, that gold, during its ſolution, takes up 43 parts *per cent.* of the oxigenous principle, and iron, though capable of taking 37, yet when newly diſſolved, takes only 27; and as it has a far greater affinity to the oxigenous principle than gold has, it takes from the ſolution of this latter, the difference between 27 and 37. And hence, to deprive the gold totally of the oxigenous principle, and reduce it to its metallic form, the vitriol ſhould be in 10 or 12 times a larger quantity than the gold.

But this anſwer is inſufficient. For, 1ſt. Copper by ſolution in acids takes up only 15,85 parts of the oxigenous principle, and yet is capable, by precipitation, of taking up 36; it has alſo, by Mr. Lavoiſier's table, p. 23, far a greater affinity to that principle than gold has, and yet the ſolution of vitriol of copper will not precipitate a particle of gold. 2d. Platina takes up a ſtill larger quantity of the oxigenous principle, and as it is inſoluble in the nitrous acid, it muſt be deemed, in the antiphlogiſtic doctrine, to have leſs affinity to that principle than nitrous air has, and conſequently its affinity muſt be very ſmall, and yet vitriol of iron in no quantity will precipitate an atom of it. The ſame reaſoning applies to the ſolutions of other metals, which have leſs affinity to the oxigenous principle than iron has, and which contain a ſmaller quantity of it than a freſh made ſolution of

iron can take up, none of which are precipitated by it in a metallic form, or at all, if the affinity of the vitriolic acid does not intervene.

Again, why iron precipitates copper from the vitriolic acid, may be explained in the antiphlogiſtic hypotheſis, ſince iron is ſaid to have a greater affinity to the oxigenous principle than copper has, and alſo to take up more of it. But why copper, which is inſoluble in the dilute vitriolic acid, ſhould become ſoluble in a dilute ſolution of vitriol of iron expoſed to the air, or in a boiling heat, ſeems to me difficult to conceive in the new hypotheſis, for the iron ſhould not only retain the oxigenous principle, with which it is far from being ſaturated, but alſo take up that which comes from the atmoſphere. Whence then does the copper attract that neceſſary for its ſolution? or if the iron divides with the copper, why does it ceaſe to be ſoluble? or if not, why does it ceaſe to be ſoluble when ſaturated with the principle of ſolubility?

3d. Iron is diſſolved by the concentrated vitriolic acid, only by the aſſiſtance of heat; yet if to a ſolution of ſilver or mercury in that concentrated acid, a piece of iron be inſerted, the ſilver or mercury will immediately be precipitated in their metallic form, and the iron diſſolved. This ſeems inexplicable in the new theory, for ſince iron cannot, without the aſſiſtance of heat, deprive ſulphur of its oxigenous principle, how does it happen, that, without that aſſiſtance, it deprives ſilver or mercury

mercury of that principle, though they have a ſtronger attraction to it than ſulphur has?

4th. Why can neither zinc, iron, or mercury precipitate tin in its metallic form, though they are ſaid to have a ſtrong affinity to the oxigenous principle, and to take up more of it than tin does?

5th. Why is regulus of antimony ſcarcely able to precipitate mercury from the vitriolic acid, though it has a greater affinity to the oxigenous principle, and takes up more of it than mercury does? On the contrary, the nitrous ſalt of mercury is eaſily precipitated by it.

6th. Why does not iron precipitate lead in its metallic form from the nitrous acid, ſince lead takes ſo ſmall a quantity of the oxigenous principle?

7th. Why does not iron precipitate lead from the marine acid, in any form?

Theſe are but a few of the many difficulties in which the antiphlogiſtic hypotheſis is involved. They are ſufficient to ſhew that its ſimplicity, though ſeducing in ſome caſes, becomes inſufficiency in many others. I paſs over many other embarraſſing objections ariſing from the precipitation of metals by different acids, as the antiphlogiſtians have not even attempted to explain any phænomena of that kind.

NOTE

NOTE.

OF

Mr. LAVOISIER,

UPON THE

Precipitation of the Metals by each other.

IN the Memoir which I publiſhed in 1782, on the Solution of Metals in the acids, I eſtabliſhed, by experiments and obſervations which have not ſince been called in queſtion, that, in every metallic ſolution, the metal is more or leſs calcined; that is to ſay, more or leſs ſaturated with oxigene, and that it obtained this principle, in ſome caſes, from the acid, and in others from the water.

In another Memoir printed the ſame year, upon the Precipitation of Metals by each other, I proved that whenever one metal was precipitated by another, and re-appeared under the metallic form, there were juſt grounds to conclude that the precipitating metal had taken the oxigene from the precipitated metal, and that by comparing the reſpective quantities of the two metals employed, a concluſion might be made of the quantities of oxigene neceſſary for the diſſolution of each metal

metal in the acids. Mr. Bergman had exhibited all theſe ſame reſults in other terms, and after the theory of phlogiſton, in a diſſertation he publiſhed upon the quantity of phlogiſton contained in metals.

Mr. Kirwan does not attack theſe principal facts, which are conſtant, and do not depend upon any hypotheſis; but he relates ſome circumſtances of the precipitation of metals which appear to him to be inexplicable upon the antiphlogiſtian hypotheſis. Before I enter into a diſcuſſion of the experiments he relates, and which he conſiders as inſurmountable objections, I ſhall proceed to lay down three principles, which appear to me to afford a ſolution before hand, of all the difficulties urged by Mr. Kirwan.

THE FIRST PRINCIPLE.

The quantity of oxigene which a metal takes, in order to become diſſolved in an acid, is not that which would be neceſſary to ſaturate it completely: it cannot take, either from the acid or the water, more than a certain quantity; the proportion of which is determined by the relative forces exerciſed upon the oxigene by the metal on the one part, and the radical of the acid on the other; ſo that when the metal is ſaturated as much as it can be in the acid or in the water, it ſtill retains an appetence for the oxigene.

THE

THE SECOND PRINCIPLE.

The force with which the oxigene adheres to a metal, is not the ſame at all the degrees of calcination. The firſt portions which it ſeizes adhere very ſtrongly, while the latter portions have very little adherence; ſo that in this kind of combinations, the affinity is a variable force, which decreaſes according to certain laws not yet determined. The ſame thing does not happen apparently in combinations which have a fixed degree of ſaturation; ſuch, for example, as in the neutral ſalts. I ſhall elſewhere give a more ample account of the phenomena which ariſe from theſe two orders of combination and ſaturation.

THE THIRD PRINCIPLE.

The affinity of the acid, whether for the diſſolved metal, or for the precipitating metal, contributes to the phenomena of the precipitation, but with much leſs energy than the affinities of oxigene.

The following details will illuſtrate theſe proportions.

If we take, ſays Mr. Kirwan, a ſolution of gold made in aqua regia, and add a ſolution of the ſulfate of iron newly made, the gold will be precipitated in the metallic form. The ſame phenomenon does not happen with a ſolution of the ſulfate of copper, or of any other metal.

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This experiment proves, agreeably to the firſt principle I have laid down, and as Mr. Kirwan himſelf ſhews, that when iron has been diſſolved in the ſulphuric acid, it is not completely ſaturated with oxigene; that it can take ſtill more; and it is not aſtoniſhing that it ſhould ſeize it from gold, to which it adheres very little. This explanation preſents nothing but what is very conformable to the known facts: the iron in diſſolving does not take, at moſt, but twenty-ſeven *per cent.* of oxigene, whether from the water or from the ſulphuric acid, and it is then in the ſtate of black oxide, or martial Ethiops: but in this ſtate it is ſtill very far from being completely calcined; if it be expoſed to the air, it can ſtill take fifteen or twenty *per cent.* of oxigene, and is then changed into yellow or red oxide. Now if the black oxide of iron can take oxigene from the air, it muſt, with much more efficacy, take it from gold, to which it has much leſs adheſion. The ſame thing ought not to happen with copper diſſolved in the ſulphuric acid, nor with the other metals, becauſe they have not ſo much affinity as iron for oxigene, eſpecially when they are partly ſaturated.

Platina, as Mr. Kirwan obſerves, has not a ſtrong affinity for oxigene, ſince it cannot be diſſolved in the nitric acid; but it has more than gold, and this is ſufficient to explain why a ſolution of ſulfate of iron does not precipitate

precipitate a ſolution of platina in aqua regia, or the nitro muriatic acid: it muſt not be concluded, that oxigene in general has leſs affinity with iron than with platina, but ſimply, that it has leſs with iron in the ſtate of black oxide, than with platina diſſolved in the nitro muriatic acid, which preſents nothing but what may be admitted. Beſides which, I have no where aſſerted, that the affinity of the acid for the precipitated metal, and for the precipitant, do not contribute to the phenomena of the precipitation; and though this cauſe acts with much leſs energy than the affinities of oxigene, it ought to enter into the explanation of the phenomena, and this is what I have expreſſed by my third principle.

Mr. Kirwan demands, why copper, which is inſoluble in the ſulphuric acid, diluted with water, becomes ſoluble in a ſolution of the ſulfate of iron, diluted with an equal quantity of water, and expoſed either to the air or to a boiling heat: I anſwer, that copper cannot be diſſolved in the ſulphuric acid, but in proportion as it is previouſly calcined, that is to ſay, oxigenated. Now as the oxigene has leſs affinity with this metal than it has with hydrogene or the baſe of inflammable gas, it cannot be calcined at the expence of the water; neither can it be calcined or oxigenated at the expence of the acid, for it has leſs affinity with oxigene than iron has; it cannot therefore, any more than that metal,

metal, become oxigenated at the expence of the diluted ſulphuric acid; whence it follows, that the copper ought to be, as in fact it is, inſoluble in the ſulphuric acid diluted with water.

But when the copper is placed in a ſolution of vitriol of iron, and this laſt is expoſed to air, it becomes more and more oxigenated, in conſequence of the well-known property of this ſolution to abſorb oxigene, or the baſe of vital air: the iron then paſſes to the ſtate of the yellow oxide, becomes ſurcharged with oxigene, and the affinity of the copper for this principle being added to that of the iron, and of the acid for the copper, ſome portions are oxigenated at the expence of the iron, and become diſſolved. The copper certainly would not take the oxigene from the iron, when in the ſtate of the black oxide; but there is no proof that it cannot take ſome portions from the yellow oxide of iron, eſpecially when it is aſſiſted by two other affinities which join in producing the ſame effect.

Mr. Kirwan likewiſe objects, that iron is not ſoluble in the concentrated ſulphuric acid, but by the aſſiſtance of heat; that is to ſay, in the antiphlogiſtic theory, it cannot take the oxigene from ſulphur, but with the aſſiſtance of heat. Now he demands, if heat be neceſſary for the decompoſition of the ſulphuric acid by iron, why this metal nevertheleſs precipitates ſilver in the cold, and mercury diſſolved

ſolved in the concentrated ſulphuric acid. I ſhall anſwer Mr. Kirwan, 1. That the heat which it is found neceſſary to employ to diſſolve iron in the concentrated ſulphuric acid, has for its object the diminution of the affinity of aggregation of the ſulphuric or vitriolic acid. One proof, that is the affinity of aggregation, otherwiſe called the attraction which the molecules of the ſulphuric acid exerciſe upon each other, which affords an obſtacle to the ſolution, is, that the ſolution takes place in whatever manner its parts are ſeparated, whether by heat, by water, or otherwiſe. Now when ſilver or mercury is diſſolved in the ſulphuric acid, the affinity of this acid is deſtroyed, and it can therefore obey its affinity for iron. Every ſtep in chymiſtry preſents examples of this kind: the metals in general are not calcined in the air, but by the aſſiſtance of heat; nevertheleſs, moſt of them are calcined in acids, without the ſame aſſiſtance: a great number of ſubſtances, which are inſoluble in the aggregate, become ſoluble when they are divided, and theſe anomalies, to make uſe of an expreſſion of Mr. Bergman, are effects of the affinity of aggregation. Beſides which, theſe difficulties are the ſame in both theories.

I ſhall reply, in the ſecond place, to Mr. Kirwan, that when ſilver or mercury, diſſolved in the ſulphuric acid, are precipitated by the intermedium of iron, this metal has no need

to decompoſe either the water or the acid, in order to become calcined: it need only take the oxigene from the ſilver or mercury, to which it adheres very little. It is not therefore aſtoniſhing that the operation ſhould be made without the aſſiſtance of heat, by virtue of the difference between this and the direct ſolution of iron in the concentrated acid, which requires the aſſiſtance of this auxiliary circumſtance.

The other objections which Mr. Kirwan makes againſt the antiphlogiſtian doctrine, and which he deduces from the precipitation of the metals by each other, are not more difficult to be explained upon the principles I have laid down; but before we enter into a diſcuſſion of the experiments he mentions, it would be neceſſary to examine how far they are exact. It would be loſt time to endeavour to explain uncertain and equivocal facts; and moreover, as I have already obſerved, proofs are not to be deſtroyed by uncertainties and probabilities. Evidence ought to be oppoſed to evidence; and all the facts which Mr. Kirwan relates in this ſection, even in avowing them, will, at the utmoſt, give birth to a few ſlight doubts, which an inſtant of reflection, and recourſe to the proofs of the antiphlogiſtian doctrine, will eaſily deſtroy.

SECT. XII.

Of the Properties of Iron in its different States, and its Converſion into Steel.

IRON ores, perfectly exhauſted of their iron by fuſion through charcoal in high furnaces, produce what is called *crude* iron, becauſe it is not malleable; being caſt in moulds, it is called *caſt* iron or *pig* iron.

The colour and properties of crude iron differ according to the proportion of the charcoal it was melted with.

If iron ores be melted with no more charcoal than is barely neceſſary for their fuſion, the crude iron will be *white*; but *grey*, if a larger proportion of coal be uſed, and if a ſtill larger *black*. The white ſort is the hardeſt, ſpecifically heavieſt, moſt brittle, and imperfectly metallized; the grey more flexible, the black the ſofteſt, but very brittle.

Malleable, or *bar iron* differs from crude iron in ſoftneſs, flexibility, and malleability, and from ſteel, in being incapable of acquiring the ſame degree of hardneſs or elaſticity by tempering: it contains leſs plumbago than either crude iron or ſteel; but when treated with acids,

acids, it gives out more inflammable air than either of them.

Steel is capable of more malleability, hardneſs, and elaſticity than malleable iron, gives out more inflammable air than crude iron, and contains leſs plumbago than crude, but more than malleable iron. The proportion of inflammable air by meaſure, in theſe 3 ſorts of iron, were found to be different both by Mr. Bergman, and Mr. Vandermond, Berthollet, and Monge, who repeated many of Mr. Bergman's experiments.

C.	Iron.	Steel.	Bar Iron.
According to Bergman, 100 gr. contain of inflam. air	40	48	50 meaſures
According to the French Academicians	54	74	76
The abſolute quantity of plumbago in 100 gr. according to Bergman	2,2	0,5	0,12 gr.

Malleable iron is convertible into ſteel, by cementation with various ſubſtances, and particularly with charcoal, in a welding heat, and by this proceſs it gains ſome weight. Hence it is plain that plumbago is a factitious ſubſtance, ſince it is formed in iron during cementation; but its production, and the properties of iron in its different ſtates, are accounted for by the antiphlogiſtians on principles very different from thoſe of Mr. Bergman, and will form the ſubject of the following diſcuſſion.

According to Mr. Bergman,* malleable iron giving out more inflammable air than ſteel, muſt contain more phlogiſton than is neceſſary to its metallic ſtate; in cementation the iron attracts the fixed air of the charcoal, which, meeting with the ſuperfluous phlogiſton, combines with it, and forms plumbago, which, like charcoal, is a compound of inflammable air and fixed air, but differs from it in this, that in plumbago both airs are more condenſed, at leaſt it forms a more compact body, and is ſpecifically heavier. Hence, 1ſt. Steel is heavier than the iron of which it was formed, having acquired fixed air. 2d. Steel gives out leſs inflammable air than the ſame weight of iron, as the ſuperfluous phlogiſton which it contained while iron, now enters into the compoſition of its plumbago, which is indecompoſable by acids.

The French Academicians, on the contrary, think† that bar iron, during cementation, abſorbs charcoal *in ſpecie*, and that this charcoal ſaturated with iron, of which it takes $\frac{1}{10}$ of its weight, becomes *plumbago*. Hence they derive the increaſe of weight in ſteel, and explain why it gives leſs inflammable air, than bar iron does. They alſo think that the inflammable air produced by ſteel, is contracted in its dimenſions by holding ſome plumbago in ſolution.

* 3 Bergm. 54. † 29 Roz. 217.

Crude

Crude iron, they ſay, contains a quantity of dephlogiſticated air; bar iron leſs; and ſteel none: if by containing a quantity of dephlogiſticated air, they meant no more than that crude iron generally contains ſome parts not thoroughly metallized, bar iron fewer, and ſteel none; it ſhould not be denied, and certainly this is all they can prove. With regard to the condenſation of inflammable air, by holding plumbago (a valuable diſcovery made by Mr. Berthollet), I muſt perfectly agree to it, as I found inflammable air extracted from black crude iron, almoſt as heavy as common air. But with reſpect to the introduction of ſo denſe a ſubſtance as charcoal into a bar of iron an inch thick, it ſeems to me very improbable; and that ſuch a ſuppoſition is uſeleſs and inſufficient, will, I flatter myſelf, appear from a review of ſome facts relative to iron in its 3 ſtates.

Facts relative to crude Iron.

Grey crude iron, melted without any addition, in a crucible, whether open or covered, is converted into ſteel. 3. Bergm. 45. This fact is equally well explained in either ſyſtem, the plumbago being decompoſed by the unmetallized part of the crude iron, which thereby becomes metallized, and only ſo much of it remaining, as is neceſſary to the ſtate of ſteel, or, according to the new theory, the charcoal being converted into fixed air by the dephlogiſticated air of the unmetallized part.

If grey crude iron be expoſed, without any addition, to a cementing, that is, a ſtrong white heat for a few days, its ſurface will be found covered with ſcales, underneath the ſurface it will be found *ſoft iron*, ſtill deeper *ſteel*, and in the center *crude iron*. Rinm. § 265. 1. Here the progreſſive deſtruction of the plumbago is well marked, in proportion to the facility with which its decompoſed airs can eſcape, and the ſtates of the iron agree with that proportion. But the antiphlogiſtic hypotheſis, which ſuppoſes pure air in crude iron and ſoft iron, cannot explain how it comes to paſs, that the ſteel, which, in this caſe, lies between both, ſhould contain none. And in fact, there is no ſort of proof that ſoft iron always and neceſſarily contains unmetallized parts.

Crude iron, cemented with charcoal, becomes more brittle. Rinm. § 265, and 266. This is conformable to both ſyſtems: but ſo it will alſo if cemented with plumbago. Rinm. 265. 21. This contradicts the antiphlogiſtic hypotheſis, for by this hypotheſis the plumbago is already ſaturated with iron, and therefore ſhould attract it no longer*.

The only proof which the French Academicians give, that crude iron contains pure air,

* Mr. Bergman, it is true, was of opinion that crude iron was not altered by cementation with plumbago. 3 Bergm. 47. But the only reaſon he gives is, that it had loſt weight; the piece itſelf was loſt before it could be further examined: why it had loſt weight is eaſily accounted for, as it muſt have loſt fixed air.

is, that having placed two pieces of crude iron in immediate contact with each other in a crucible, and ſurrounded them with charcoal, after a few hours expoſure to heat, they increaſed in weight; but the ſurfaces in contact with each other were calcined. But this experiment proves no more, than that crude iron is not perfectly metallized, but contains ſome particles in a calcined ſtate, and that the internal parts give out fixed air or water, which calcines the ſurfaces not in contact with the charcoal.

Facts relative to malleable Iron.

IF malleable iron be ſurrounded with charcoal in a covered crucible, and expoſed to a welding heat for 8 or 10 hours, it will be converted into ſteel, as is well known; but if the experiment be made in a glaſs veſſel hermetically ſealed, this converſion will not take place in any length of time or degree of heat. Rinm. § 267, N. 7. This is inexplicable in the antiphlogiſtic theory, for the charcoal ſhould equally be abſorbed, whether the veſſel be hermetically cloſed or not. But in Mr. Bergman's it is eaſily explained, for the charcoal cannot be decompoſed, unleſs the inflammable air be at liberty to aſſume an aerial form; juſt as vitriol of iron will remain in contact with an aerated alkali, without expelling the fixed air, or any union of the acid and alkali, when both are diſſolved in a veſſel well cloſed*,

* See Lewis on 1 Newm. p. 272.

and as light will not ſeparate pure air from nitrous acid in a veſſel perfectly full and cloſed.

If a bar of ſoft iron be put into a crucible well covered and luted, without any addition, and kept in a welding heat for 11 days, it will be converted into ſteel, its ſurface covered with plumbago, and it will weigh about 1 per cent more than before. Rinm. § 73. xviii. Here it is plain the charcoal could not penetrate through the crucible, but fixed air eaſily can, as it is well known that crucibles in a white heat are pervious to air. The plumbago then clearly owes its origin to this air, as Mr. Bergman explains it.

Mr. Rinman alſo cemented bar iron with *chalk*, and after keeping them 11 days in a welding heat, he found the iron converted into ſteel, and covered with plumbago. It is true, he ſays, the effect was the ſame, when, inſtead of chalk, he uſed quick-lime; but it is probable the lime he uſed on this occaſion was not well burned, for, at another time, when he uſed, as he expreſsly ſays, lime perfectly burned, though it had been expoſed to the air half a year, ſo far from converting the iron into ſteel, it rendered it perfectly ſoft. When iron was cemented with chalk for 3 hours only, it had no effect upon it, as it could not give out its air in ſo ſhort a time; on the contrary, the iron loſt part of its weight. § 73. ix. Here alſo we ſee plumbago formed without charcoal.

Bar

Bar iron cemented with the black calx of manganeſe, was not calcined as it ſhould be, according to the antiphlogiſtic theory, but on the contrary, converted into ſteel. Rinm. § 73. xvii. The reſult was the ſame when it was cemented with flowers of zinc, and the zinc was reduced to its metallic form. Ibid. iii. Which laſt circumſtance contradicts Mr. Lavoiſier's table: plumbago appears in both caſes to have been formed without charcoal.

Malleable iron cannot be melted in furnaces without addition; but if it be ſurrounded with charcoal, it firſt becomes ſteel, then crude iron, and at laſt melts: this crude iron ſurely contains no unmetallized parts.

Facts relative to Steel.

THE French Academicians ſay, that if crude iron be long kept in fuſion in a covered crucible, it will at laſt be reduced to the ſtate of malleable iron; but ſteel in the ſame circumſtances will remain unaltered. Hence they infer that crude iron contains ſome principle which deſtroys the charcoal, namely, pure air, but that ſteel contains none*. Yet Rinman expreſsly ſays that ſteel alſo, by long continued fuſion, will become malleable iron, § 266; and in their own experiment crude iron muſt paſs through the ſtate of ſteel before it arrives at that of malleable iron.

* 29 Roz. 217.

If

If ſteel be cemented with quick-lime, it will be converted into malleable iron, becauſe by the affinity of quick-lime to fixed air, the plumbago is more eaſily decompoſed; but by cementation with calx of zinc, it is not altered, Rinm. § 73; becauſe ſteel contains no ſuperfluous phlogiſton. According to the antiphlogiſtic theory, the pure air of the calces ſhould deſtroy the plumbago.

Thence we ſee that the new theory explains no incident or property of iron which is not as well explained without it; on the contrary, Mr. Bergman's theory elucidates facts, which the new theory leaves in obſcurity.

To the proofs which Mr. Scheele has given that plumbago conſiſts of inflammable air and fixed air in a concrete ſtate, I ſhall add one more reſulting from Mr. Pelletier's experiments*. If plumbago be diſtilled with dry cauſtic alkali in a pneumatic apparatus, it will yield inflammable air, and the alkali will become aerated.

* 27 Roz. 352.

NOTES

NOTES

BY

Mr. MONGE,

Page 259. line 17.

OUR Memoir on the Properties of Iron is not yet printed, and is no otherwiſe known to the public than by an extract inſerted in the Journal de Phyſique, by Mr. Haſſenfratz. Mr. Kirwan therefore cannot be perfectly acquainted with our labour, nor the manner in which we explain the different phenomena which are preſented by iron.

It might be imagined, from the quotation here referred to, that the volumes of hydrogenous gas which we obtained by the ſolution of caſt iron, ſteel, and malleable iron, are always, at leaſt nearly, in the ratios of the numbers 54, 74, and 76; but nothing can be farther from what we have aſſerted in our Memoir. Soft iron, perfectly reduced and entirely deprived of plumbago by refining, ſuch as is nearly the beſt Swediſh iron, is the only one of the three metallic ſubſtances we treat of, which affords and can conſtantly afford the ſame volume of hydrogenous gas by its ſolution in the ſulphuric acid, becauſe it is the only

only one which is conſtantly in the ſame ſtate: we found that 100 grains of this iron afford 78 meaſures of hydrogenous gas, meaſured under a preſſure of 28 inches of mercury, and at a temperature of 22 degrees of a thermometer, divided into 80 parts, from the freezing point to that of boiling water. On the contrary, the ſteels being capable of variations in the quantity of plumbago they may contain, and the ſpecimens of caſt iron being ſuſceptible of differences, not only in the quantity of plumbago, but likewiſe in the point to which the reduction of metal is carried, the volumes of hydrogenous gas obtained in the ſolutions of the ſubſtances, do vary conſiderably according to circumſtances; ſo that the grey caſt iron which cannot be obtained but by augmenting the doſe of charcoal in charging the furnace, and which, having been expoſed to a more elevated temperature, is carried to a higher point of reduction, and in this reſpect approaches nearer to the ſtate of ſoft iron, conſtantly diſengages more hydrogenous gas than the white caſt iron, in the fabrication of which leſs charcoal has been uſed, and whoſe reduction is much leſs advanced.

For example, we have found that the grey caſt iron of the royal forges of Guerigny affords 71 ounce meaſures of hydrogenous gas; that the iron produced from this metal affords 76; and that the ſteel produced from this iron affords 74, though neither the white caſt iron

of

of Huttemberg, nor that of Wolfsberg, afford more than 60.

It muſt be well obſerved, that in this place we uſe the words white caſt iron, *(fonte blanche)* to imply that which is ſuch when it comes out of the high furnace, and not that which, after having been of a grey colour, may have been whitened by one or more fuſions in reverbertory furnaces. For when the grey caſt iron is fuſed again by a very ſtrong heat, the plumbago, that is to ſay the carbure of iron which it contained, and which gave it its colour, is employed in advancing the reduction, and diſappears either wholly or in part; the caſt iron which is thus obtained muſt afford more hydrogenous gas than the grey caſt iron from which it was produced, becauſe its reduction is farther advanced; it ought, even at equal ſtates of reduction, to afford a greater volume than any other grey caſt iron; 1. Becauſe, containing leſs plumbago, it includes more metallic parts under the ſame weight; 2. Becauſe the plumbago of the grey caſt iron becomes diſſolved in the hydrogenous gas, and diminiſhes the volume of elaſtic fluid.

Page 261. line 1.

WE affirm that malleable iron, perfectly refined, is the metal, not only reduced in a complete manner, and conſequently deprived of all the oxigene with which it was combined in the ore, but likewiſe deprived of all the carbone which it abſorbed in the ſmelting furnace;

furnace; that is to ſay, as well from that which remained ſtill combined with the crude metal, as of that which was abandoned in the form of plumbago on account of the cooling, and which having been afterwards ſurpriſed by the hardening or congelation of the metal, remained diſſeminated through its maſs. The general proceſſes for refining iron are all directed towards this triple depuration; but the low price of the metal does not admit of employing theſe proceſſes but in a groſs manner, and all the iron in commerce contains a quantity of oxigene and carbone, though indeed very ſmall; the ſofteſt and moſt flexible forged irons, ſuch as thoſe of Sweden, contain leſs both of the one and of the other of theſe two ſubſtances.

In the ſteel of cementation the metal is perfectly reduced, becauſe the temperature neceſſary to the combination of carbone with the iron is much higher than is ſufficient for the complete reduction.

We have not therefore intended to ſay, that oxigene was neceſſary to ſoft iron; we have on the contrary affirmed, that iron is the ſofter the leſs oxigene it contains.

Page 261. line 3.

THE proceſſes which are followed in the furnaces, are not ſuſceptible of preciſion enough that the caſt iron either can or ought to be regarded as a homogenous ſubſtance; ſo that, as Mr. Kirwan obſerves, the molecules of

of crude iron are not all equally metallized. But we affirm more: when even theſe proceſſes are very exact, and when the crude iron is, at leaſt in the fluid ſtate, a ſubſtance perfectly homogenous; from the very circumſtance that it was ſtill crude iron, it would ſtill contain oxigene; that is to ſay, the reduction would be every where begun, every way carried to the ſame degree, but completed in no one part of the maſs. It is by this reſidue of oxigene that crude iron differs from refined iron when it does not contain plumbago, and in which it differs from ſteel of cementation when it does contain that ſubſtance; it is by the quantities of oxigene that the white crude irons differ from each other, and the principal proceſſes for refining them tend to the ſingle object of depriving them of it.

This aſſertion is obviouſly conformable to the nature of things; it is fact proved, that oxigene may be combined with iron in all proportions: for example, the ethiops, or black oxide of iron, which Meſſrs. Lavoiſier and Meuſnier have obtained by calcining iron by the vapour of water, is evidently a middle ſtate of iron between that of oxide or martial calx and that of refined iron; that is to ſay, that in this ethiops, which is in other reſpects a homogenous ſubſtance, the calcination is every where begun, every where carried to the ſame degree, but in no part to its ex-

treme term. Now the firſt particles of oxigene which combine with iron, adhere to it with more force than thoſe which enter later into the combination. Thoſe circumſtances therefore, ſuch as the temperature, the quality of the coal, &c. which were ſufficient merely to deprive the iron of thoſe particles of oxigene which adhere leſs ſtrongly, could not deprive it entirely of that principle, and conſequently the reduction muſt have begun every where, but in no part be completed.

It is not enough to ſhew that our aſſertion is plauſible; it is likewiſe neceſſary to prove, from obſervations, that it is well founded.

We cannot here urge, as a proof, the difference of the quantities of hydrogenous gas diſengaged by the ſolutions of refined iron and caſt iron in the acids, nor that which ariſes from the ſolution of different ſpecimens of white crude iron, becauſe Mr. Kirwan, who conſiders crude iron as a mixture of particles of iron perfectly reduced, and others not entirely metallized, might attribute the inequalities to the different proportions of the reduced and unreduced parts: but we ſhall obſerve—

1. That all the ſamples of white crude iron, which are deprived of plumbago, are ſuſceptible of a perfect cryſtallization, and may be regarded as ſubſtances ſenſibly homogenous.

2. That when the degrees of reduction of

two

two molecules of the ſame metal are very different, theſe molecules have no longer any ſenſible affinity for each other, and can no longer combine together without an intermedium; for example, the ethiops of Mr. Lavoiſier, which may be obtained as well from refined iron as from white crude iron, does not adhere to either of theſe two laſt ſubſtances; the red oxide on its part does not adhere to either of the three; it would not therefore be practicable with the oxide, the ethiops, the white crude iron, and refined iron, to form a ſubſtance ſo homogenous as the caſt iron, and ſuſceptible of a regular and determinate cryſtallization, unleſs the exceſs of oxigene contained in the oxide and ethiops were tranſmitted to the crude and the refined iron, to bring the whole to a mean and uniform ſtate of reduction.

3. When white crude iron is fuſed again in the pots of the refinery, and is expoſed by agitation of its parts to the contact of charcoal, the portions which by this contact have been entirely or almoſt entirely reduced, become infuſible, and take the form of a paſte. The maſs is then in the ſtate which Mr. Kirwan ſuppoſes, that is to ſay, it is compoſed of crude and of malleable iron; but likewiſe, if this maſs be ſuddenly cooled and then broken, it is eaſy, by the fracture and the cryſtallization, to diſtinguiſh the reduced iron from that which is not reduced; their aſpects differ as

well as their nature, and the cryſtallization is not uniform, like that of the crude iron.

4. When the refiner plunges a bar of forged iron, ſuch for example as a ringard, into the fuſed white crude iron, leaving it there for ſome time without agitation, and afterwards takes it out, it is enveloped with a covering more or leſs thick of refined iron, which may be taken off and hammered out into a bar. In the opinion of Mr. Kirwan, it muſt be ſuppoſed that the reduced parts of the crude iron, attracted at a diſtance by the bar, came to adhere to it notwithſtanding the great reſiſtance of the fluid metal; which on the one hand would be contrary to ſound philoſophy, and on the other would not be conformable to the facts, for the coating does not adhere to the bar. We ſee clearly in this phenomenon, that the refined iron of the bar, whoſe affinity for oxigene is greater than that of the crude iron at an high temperature, deprives the circumambient crude iron of a great part of the oxigene it retained, and brings it to a ſtate of reduction, which renders it infuſible and extenſible under the hammer.

We are therefore authorized to conſider white crude iron as a homogenous ſubſtance; as a metal whoſe reduction is every where advanced nearly in an uniform manner, or, in a word, as iron which is in a mean ſtate between iron completely refined and deprived of oxigene, and the red oxide which is ſaturated with this laſt ſubſtance.

Page 261. line 10.

WE have not ſaid that hydrogenous gas can hold plumbago in ſolution, but merely that it can diſſolve carbone. This difference, which may be ſaid to be none with reſpect to Mr. Kirwan, is very conſiderable in our ideas, becauſe that we believe that iron is eſſential to plumbago. With regard to the contraction which hydrogenous gas undergoes in diſſolving carbone, the diſcovery is not due to Mr. Berthollet excluſively; it belongs to us in common, like the reſt of the work; but we are indebted to Mr. Berthollet for the preceding experiments which he made alone, and to which we had recourſe to verify this phenomenon, when we merely ſuſpected it.

Page 261. line 30.

IN this experiment, part of the carbone, by combining with the reſt of the oxigene which is in the crude iron, completes the reduction of the metal, and forms carbonic acid gas, which cauſes a kind of effervescence; the other remaining part combining with the iron, gives the metal the characters of ſteel.

Page 262. line 11.

Mr. Kirwan is conſtantly in an error with regard to our opinions; he thinks that we admit oxigene as eſſential to ſoft iron, where-

as, on the contrary, we affirm that iron is not perfectly ſoft unleſs it be entirely deprived of oxigene. The operations of refining, all tend to deprive it of this ſubſtance; but we have ſaid that theſe operations were not performed with ſufficient accuracy to complete the depuration, and that the beſt iron in commerce ſtill contained a ſmall portion of oxigene. Hence the phenomenon here ſpoken of is eaſily accounted for, if it has been well obſerved; but in the order of the ſubſtances here obſerved, the name of ſteel was applied to a grey crude iron, whoſe reduction was more advanced, and which differed very little from natural ſteel; whereas we underſtand by ſteel, that which is made by cementation, and is always in a ſtate which, if not more conſtant, is at leaſt more uniform.

Page 262. line 23.

IN plumbago at low temperatures, the carbone may be ſaturated with iron without this ſaturation ſubſiſting at the temperature of crude iron in fuſion. Every thing leads us to think, on the contrary, that the affinity of carbone for iron encreaſes very rapidly as the temperature is raiſed. There is nothing therefore in this phenomenon which contradicts our manner of explaining the facts; it confirms it, on the contrary, for in order to convert iron into ſteel by cementation with plumbago,

plumbago, it is neceſſary to expoſe it to a much ſtronger heat, continued for a longer time, than if the cement conſiſted of pure charcoal; which ariſes from the affinity of the carbone for iron being diminiſhed by the portion of that metal to which it is already united in the plumbago.

Page 262. line 26.

WE do not recollect the experiment Mr. Kirwan here ſpeaks of. But the proofs of the exiſtence of oxigene in caſt iron are numerous; the principal are, 1. That by its ſolution in the ſulphuric and muriatic acids, crude iron conſtantly diſengages leſs hydrogene than ſoft iron. 2. That by virtue of the temperature only, the grey crude iron is refined, and becomes white without addition and without the contact of air, while the ſteel of cementation, which does not contain oxigene, will ſuſtain the higheſt temperatures in cloſe veſſels, provided it be defended from the contact of the air. Other proofs may be ſeen page 279.

Page 263. line 17.

WE do not underſtand this experiment. The temperature neceſſary for the cementation of iron being much higher than that which ſoftens and melts glaſs, if the veſſel was not fuſed, the heat could not have been ſtrong enough to have effected the cementation.

Page 264. line 15.

THIS experiment is entirely different to that of Mr. de Reaumur, who, on the contrary, by cementing ſteel in chalk, in quick-lime, in powder, in calcined bones, and in general in all kind of incombuſtible and infuſable powders, conſtantly brought it to the ſtate of iron, becauſe theſe powders permit the acceſs of air, and give place to the decompoſition of the plumbago.

Page 265. line 1.

WE have every reaſon to believe this experiment to be inaccurate.

Page 265. line 11.

WE have well diſtinguiſhed four different ſtates of iron. 1. The ſtate of crude of caſt iron, in which the metal is when it flows out of the ſmelting furnace. 2. That of refined iron. 3. That of ſteel of cementation. 4. That of ſteel too much cemented and very fuſible. It is to this laſt ſubſtance which Mr. Kirwan here gives the name of crude iron, and confounds it with the product of the furnace. Crude iron contains oxigene, becauſe the reduction could not be completed in the furnace, and ſteel too highly cemented does not contain it, becauſe the heat neceſſary to cementation is higher than that which operates the complete reduction of the metal.

Page

Page 265. line 24.

IN order that ſteel may not experience any alteration by expoſure to a long continued heat, it is neceſſary that it ſhould be entirely defended from the contact of the air: but if it be in a veſſel ſimply covered, as Mr. Kirwan mentions, and into which the air of the atmoſphere can have acceſs, its plumbago burns, and it paſſes ſlowly to the ſtate of ſoft iron. Moreover, we have not ſaid that crude iron muſt paſs through the ſtate of ſteel to become malleable iron; on the contrary, in order to obtain the ſteel of cementation, the firſt ſtep is to refine the crude iron, and convert it into malleable iron, after which the iron is ſubjected to cementation.

Page 266. line 5.

WE have not repeated this experiment of Mr. Rinman, but, if it be accurate, it proves only that plumbago engaged in a maſs of ſteel, and ſeparated from the oxide of the zinc by the molecules of this maſs, cannot take the oxigene from the oxide; which it would do if it were in contact with it.

Page 266. line 10.

OUR Memoir will appear in the volume of the Academy of Sciences for the year 1786; when it ſhall be publiſhed, and Mr. Kirwan

ſhall become acquainted with our experiments: we preſume to think, that the manner in which we render an account of all the properties of iron, and of a great number of obſervations, which were before unknown to chymiſts, will appear ſatisfactory to him.

Page 266. line 20.

THERE is no doubt but the alkali of Mr. Pelletier, though dried by the uſual methods, contained water which was decompoſed.

SECT.

SECT. XIII.

Concluſion.

THE patrons of the new theory agree, that metallic inflammable air, uniting to pure air in a red heat, produces water.

2dly. That ſpirit of wine, during its inflammation, produces both fixed air and water. Mr. Lavoiſier even found that the quantity of water left after the combuſtion of ſpirit of wine was ſo great as to exceed the original weight of the ſpirit, which ſhews it muſt have contained a large quantity of phlogiſton.

3dly. That oils and reſins alſo contain inflammable air, and conſequently during combuſtion produce both water and fixed air.

4th. That both inflammable air and pure air give out fire during their inflammation.

But ſulphur, phoſphorus, zinc, and regulus of antimony, to mention no other, alſo inflame, in common air, as does iron in dephlogiſticated air; therefore, according to the rule which requires that *to natural effects of the ſame kind, the ſame cauſe ſhould be aſſigned*, we are led to conclude, that the flame in this caſe

alſo

alſo proceeds from the union of inflammable air and pure air, unleſs it ſhould be proved that thoſe ſubſtances contained no inflammable air, which has not yet been done: all that the antiphlogiſtians ſay, amounts to no more, than that inflammable air is not neceſſary, ſince dephlogiſticated air gives out fire enough, a reaſon ſufficiently refuted by the inflammation of ſpirit of wine and oils.

Again, volatile alkalis confeſſedly contain inflammable air, and though they hardly detonate with melted nitre on account of their volatility, yet ſal ammoniac, and particularly vitriolic ammoniac, being more fixed, readily makes nitre detonate; but ſubſtances which confeſſedly contain no phlogiſton, or hardly any, as ſtones, glaſs, metallic calces, &c. will not make nitre detonate. Hence we are authorized to conclude that other ſubſtances which make nitre detonate, contain phlogiſton, unleſs the contrary be ſhewn; now ſulphur, charcoal, and moſt of the imperfect metals detonate with nitre, and hence we have a ſecond reaſon deduced from analogy to conclude that they contain phlogiſton.

Further, if nitrous ammoniac be projected into a red hot crucible, nitrous air is produced; if nitrous acid be digeſted with ſpirit of wine, nitrous air is alſo produced; therefore, in other caſes where we ſee nitrous air produced, we are authorized to think that phlogiſton is preſent; now ſulphur, phoſphorus, and metals

treated

treated with nitrous acid afford alſo nitrous air, we have then a farther reaſon to conclude they contain phlogiſton.

Therefore when we ſee inflammable air proceed from the ſolution of metals, or by paſſing the ſteam of water through them, or through ſulphur, it is much more reaſonable to infer that it proceeds from the metals and ſulphur than from the decompoſition of water, of which we have not a ſingle undoubted inſtance.

To the proofs I have heretofore given that inflammable air and phlogiſton are the ſame ſubſtance, juſt as ice and the vapour of water are called the ſame ſubſtance, no objection of any weight has ſince been made. Some have thought I ſhould have included the matter of heat or elementary fire in the definition of inflammable air, but as fire is contained in all corporeal ſubſtances, to mention it is perfectly needleſs, except where bodies differ from each other in the quantity of it they contain, and in this reſpect I expreſsly mentioned its difference with phlogiſton to conſiſt. Others attending to the quantity of water contained in inflammable air, have ſuppoſed it to be an eſſential ingredient in the compoſition of this air, and have called it *phlogiſticated water*; but they may as well ſuppoſe water to be an eſſential ingredient in common air or fixed air, and call this laſt *acidulated water*; for inflammable air, equally as other airs, may be

be deprived of its water without any limitation, and yet preſerve all its properties unaltered, which ſhews the preſence of water to be no way eſſential to it. Laſtly, others have thought that it eſſentially requires an acid or an alkali, or ſome ſaline ſubſtance for its baſis, as if there were any more repugnance in the nature of things that phlogiſton ſhould exiſt in an aerial ſtate without any baſis, than marine air, or alkaline air, or dephlogiſticated air, &c. when it is evident that an aerial ſtate requires no more than a certain proportion of latent heat; but the production of inflammable air from iron by means of diſtilled water without any acid or ſalt, has effectually done away every ſuſpicion of this ſort.

The End of Mr. KIRWAN's Eſſay.

NOTE

NOTE

OF

Mr. DE MORVEAU,

UPON THE

CONCLUDING SECTION

OF

Mr. Kirwan upon Phlogiſton.

Page 281.

MR. Kirwan admits, with us, that inflammable air produces water by uniting with pure air at a certain heat: he admits that the principle which forms its baſe needs only heat to exhibit itſelf in the ſtate of gas, that it does not eſſentially contain either water, acid, or ſalt; he admits, as we do, its preſence in volatile alkali, ſpirit of wine, oils, and reſins; he equally agrees with us, that the acids do not exiſt ready formed in ſulphur, phoſphorus, nitrous gas, &c. but that pure air enters into the compoſition of theſe acids, as well as into that

that of the metallic oxides, conformably to the new theory.

He departs, then, from this doctrine in three points only.

1. Inflammable gas exiſts likewiſe in ſulphur, phoſphorus, nitrous gas, &c. in the ſtate in which it has been called the phlogiſtic principle.

2. It exiſts likewiſe in the metals and in charcoal.

3. By uniting to pure air, it forms fixed air; and it is not till after this compoſition that the air becomes the acidifying principle, and a conſtituent part of metallic oxides.

Theſe three propoſitions, which form the baſis of the author's own ſyſtem, abſolutely depend on the proofs of the exiſtence of phlogiſton, or, if it be ſo taken, of inflammable gas in thoſe ſubſtances. The author has been well aware of this, and has reſumed it in his concluſion, to place in the ſtrongeſt light ſuch of his proofs as appear to him to be moſt concluſive; and thence it is that we ſhall take them, in order to examine them.

The arguments condenſed in this laſt ſection may be reduced to four.

ARGUMENT THE FIRST.

NATURAL effects of the ſame kind ought to be attributed to the ſame cauſe; now the combuſtion of ſulphur, phoſphorus, zinc, &c. is

of

of the ſame kind as that of inflammable gas: it therefore depends on the ſame cauſe.

ARGUMENT THE SECOND.

NITRE detonates with volatile alkali, and the other ſubſtances which are known to contain inflammable gas; it does not detonate with ſtones or the metallic oxides, which are known not to contain it. There is therefore reaſon to think, that all bodies which detonate with nitre contain inflammable gas.

ARGUMENT THE THIRD.

NITROUS gas is obtained by projecting amoniacal nitre in a red hot crucible, it is obtained by digeſting the nitric acid upon ſpirit of wine, and it is known that volatile alkali and ſpirit of wine contain inflammable gas: ſulphur, phoſphorus, and the metals likewiſe afford nitrous gas when treated with this acid: it may therefore be concluded, that they likewiſe contain inflammable gas.

ARGUMENT THE FOURTH.

SINCE inflammable gas is produced during the ſolution of metals, in the ſame manner as when water is made to paſs in vapour over the metals and over ſulphur, it is more reaſonable to think that this gas comes from theſe bodies than from the decompoſed water.

Before we examine each of theſe arguments ſeparately, we ſhall make two general obſervations, which appear to us to be of great importance: the firſt is, that by the author's own acknowledgment, they do not demonſtrate either the neceſſity or the reality of the exiſtence of phlogiſton, or of inflammable gas, in the bodies wherein it was propoſed to demonſtrate its being, ſuch as ſulphur, phoſphorus, charcoal, the metals, the nitrous gas, and that all the concluſions are by analogy only.

We ſay, that by the author's own acknowledgment, the concluſions are by analogy only; which reſults evidently from theſe terms, by which he modifies the conſequences, "unleſs it ſhould be proved that thoſe ſubſtances contained no inflammable air"; for there is no one who does not conceive that this reſerve of the poſſibility of a contrary proof is abſolutely repugnant to the idea of a direct and formal proof.

The ſecond obſervation is, that according to the rules of accurate logic, there can ſtrictly be no negative proofs, or proofs of a negative fact, becauſe a fact of this kind does not neceſſarily exclude the poſitive fact; whence it follows, that the non-exiſtence of phlogiſton is ſufficiently proved by the want of proofs of its exiſtence, or at leaſt there is no reaſon to admit it until we have poſitive proof of the neceſſity of its preſence.

Let us now reſume the arguments ſeverally.

CON-

CONCERNING THE FIRST ARGUMENT.

THE firſt of the preceding obſervations applies very well to this argument; to ſay that effects are of the ſame kind, does not imply that they are produced by the ſame ſubſtance; the difference is ſenſible: the firſt propoſition affirms a pure analogy, the ſecond was the only one from which an inference could be drawn of the exiſtence of inflammable gas in all combuſtibles; the argument therefore proves nothing; the ſolution of ſoda, for example, in the ſulphuric acid, is indeed an effect of the ſame kind as its ſolution in the muriatic acid, and moſt certainly that does not prove that theſe two acids are one and the ſame acid.

So that we might admit the three propoſitions of the argument without being able to draw any further conſequence; but to give a more direct ſolution, it will be ſufficient to determine preciſely the analogy between all combuſtions, and what conſtitutes them effects of the ſame kind: we ſoon ſee that there is no other circumſtance than the decompoſition of vital air, by the ſuperior affinity of any ſubſtance, by means of which the heat, previouſly combined in this vital air, becomes diſengaged and ſenſible. This is what brings all combuſtions into one claſs, and this by no means decides that there is only one ſubſtance capable of exerciſing this affinity. We aſſert that there are no other circumſtances, and this

propoſition is demonſtrated by the difference of the products of the combuſtion; for the acid left by the combuſtion of ſulphur is very different from that which the combuſtion of charcoal affords; the reſidue of the combuſtion of inflammable gas is ſtill more different from the reſidue of the combuſtion of zinc, phoſphorus, &c. But if it be a conſtant truth, that the ſame body when decompoſed by the ſuperior affinity of the ſame ſubſtance, can never afford any other than one and the ſame product, what ſtronger proof can be deſired, that in the preſent caſe there are different matters which exerciſe this affinity upon the baſe of vital air.

It is therefore in this ſenſe, and in this ſenſe only, that vital air is always decompoſed in combuſtion, that it can be affirmed that all combuſtions are referable to one and the ſame cauſe, and the identity of the matter which effects this decompoſition depends on nothing more than begging the queſtion, or a gratuitous ſuppoſition. If we wiſh to confine ourſelves to the facts, we ſhall ſay with the antiphlogiſtians: it is univerſally admitted that ſulphur, charcoal, the metals, &c. are different ſubſtances; it is equally admitted that theſe ſubſtances decompoſe vital air in combuſtion: therefore vital air can be decompoſed by different ſubſtances.

This conſequence will, no doubt, appear rather more ſtrict than thoſe we are now examining.

UPON THE SECOND ARGUMENT.

THE ſecond argument is likewiſe nothing more than a concluſion founded upon a ſuppoſed analogy, and which remains without probability, when the phenomena are explained without the aſſiſtance of any hypotheſis. Now it is evident that the detonation of nitre is performed, like combuſtion, by the means of a body which has a greater affinity with the baſe of vital air than the azote or nitrous gas has, which at a certain degree of heat can decompoſe the nitrous acid by virtue of this affinity; this is a more certain analogy, and is proved by the fact itſelf. Hence it follows, that it is not one ſingle ſubſtance, but every body poſſeſſing this affinity, which determines the detonation as well as the combuſtion; that the reſidue after the operation, or the product of the detonation, muſt vary according to the nature of the body employed, in the ſame manner as in combuſtion; in a word, that this affinity muſt ceaſe when the body is previouſly ſaturated, as in the metallic oxides; and the whole is explained in a more ſimple manner without any hypotheſis.

If another proof of this laſt analogy be required, the decompoſition of the nitric acid, by the humid way, affords it: for phoſphorus, arſenic, and charcoal itſelf, decompoſe the nitric acid at a low heat; they are found afterwards in the ſame ſtate of compoſition as if they had been burned in vital air; the detona-

tion therefore is really no more than the reſult of the affinity, by which any ſubſtance deprives the nitric acid of its vital air, diſengages heat, fixes the baſe of this air in new combinations, and forms different compounds according to the different ſubſtances which exerciſe this affinity.

Moreover, the ſyſtem of the learned Academician of London here preſents a difficulty, of which he does not ſeem to have been aware, though it is of ſome importance. If we aſk him why a metal calcined, for example in vital air, does not cauſe nitre to detonate, ſince by his principles the metallic oxide ſtill contains phlogiſton, we may foreſee his anſwer, That the phlogiſton being actually ſaturated with vital air, can no longer exhibit any affinity towards it. But when we again demand in what manner he conceives that this calcined metal can be reduced; he ſurely will not ſay that it is by virtue of the affinity which the added phlogiſton will exerciſe upon the vital air; becauſe it is agreed that this action is repugnant to the idea of a pre-exiſtent ſaturation by the ſame principle. It cannot therefore take place but by the affinity of the newly added phlogiſton with the metal; now in this caſe, whatever ſubſtance be employed for the reduction, the products ought always to be on one ſide the reduced metal, and on the other all the carbonic acid, which put it into the ſtate of calx; this does not happen: therefore

therefore the reducing ſubſtances do not act as pure phlogiſton, and conſequently they exerciſe their action upon the vital air.

We ſay, that this does not happen; it is known that no carbonic acid is afforded in reductions, except when the acidifying vital air is reſumed by charcoal, and that its quantity when produced, is in proportion to the ſmall quantity of charcoal which the vital air ſometimes accidentally meets with. The latter experiments of Dr. Prieſtley have put theſe truths out of all doubt *. He calcined iron in vital air by the burning glaſs; he reduced it by means of very dry hydrogenous gas upon very dry mercury; he found water in a quantity correſponding to the weight which the iron had loſt, and to the weight of gas abſorbed; the remainder was hydrogenous gas as before, and did not contain any fixed air at all.

We do not apprehend that a ſtronger demonſtration can be expected, that hydrogenous gas and charcoal are not identical ſubſtances, and that phlogiſton in theſe operations acts a part which is ſuperfluous, and purely hypothetical.

It would be in vain to attempt to elude the conſequence of this experiment of Mr. Prieſtley, by ſaying that in this caſe the carbonic acid, which placed the iron in the ſtate of metallic oxide, has been converted into water

* Experiments and obſervations, vol. 3. page 82.

during its reduction by hydrogenous gas; the poſſibility of this converſion of the carbonic acid into water is no where proved; it may even be affirmed, that all the known facts oppoſe this opinion: in a word, it is much rather a new difficulty in the hypotheſis of our author, than a general ſolution of all the objections which may be made againſt it, that he is under the neceſſity of admitting, as we have ſeen, that phlogiſton or inflammable gas and vital air conſtitute almoſt at pleaſure alone, without any other modifying ſubſtance, water, carbonic acid, the acidifying principle, and the nitric radical, which nevertheleſs ſhew themſelves to be ſo different, as well in their properties, as in the products they form by combination.

UPON THE THIRD ARGUMENT.

ADMITTING that it had been previouſly eſtabliſhed, that nitrous gas could not be formed but by the means of phlogiſton, this argument would be ſufficient indeed to conclude that all the ſubſtances which give riſe to its formation contain phlogiſton; but thus far the very exiſtence of this principle is left a matter of diſpute.

Moreover, if nitrous gas be one of the conſtituent parts of the nitric acid, as is proved by the regeneration of this acid, by the direct combination of nitrous gas with vital air, it is not

not at all ſurprizing that every ſubſtance which is capable of reſuming the vital air, ſhould always leave its acidifiable baſe in the ſame ſtate of nitrous gas. We have already ſhewn, that it is not hydrogenous gas which alone poſſeſſes this property, but that it is common to moſt combuſtible ſubſtances, and that the evident proof of the different nature of theſe ſeveral ſubſtances is derived from the variety of the products of their union. Now this variety is ſhewn in all the operations wherein nitrous gas is collected, abſolutely in the ſame manner as in combuſtions; theſe products are, according to the ſubſtances uſed in diſengaging nitrous gas, either phoſphoric acid, arſenical acid, a metallic oxide, &c. &c.

Laſtly, we find the ſame difficulty here which appears to accompany the hypotheſis of Mr. Kirwan in all its applications. When we burn, for inſtance, phoſphorus in vital air, the affinity of decompoſition, or that which exerciſes the firſt action, is not in this ſyſtem the direct affinity of vital air with the phoſphorus; for it is required that the baſe of vital air, and the phlogiſton of the phoſphorus, ſhould firſt form the acidifying principle. On the contrary, when phoſphorus is converted into phoſphoric acid by means of the nitric acid, it is the fixed air or acidifying principle, ready formed in this laſt, which attacks the phoſphoric radical, while the

phlogiſton of the phoſphorus unites to the nitric radical.

It is neceſſary therefore to ſuppoſe further, though we have hitherto no appearance of any ſuch thing, that the phoſphorus can be converted into an acid by the union of fixed air ready formed; that this can happen at leaſt by the way of double affinity; and that in all acidifications the phlogiſton of the acidifying body is always found in a quantity preciſely equal to what the ſaturation of the nitrous gas requires, ſince after the operation we obtained neither diſengaged phlogiſton, nor the nitric radical in a different ſtate from that of nitrous gas. It is not, as we ſee, but by accumulating ſuppoſitions that the difficulties of the original hypotheſis are eluded.

UPON THE FOURTH ARGUMENT.

THAT the hydrogenous gas, diſengaged from metals during their ſolution in acids, or when they are ignited and expoſed to the vapour of water, comes rather from the metals than from the decompoſed water, is much leſs, even in the terms of the author, a new fact, which he thinks himſelf capable of proving, than a probability deduced from the preceding arguments; and for this reaſon we have obſerved, that in the ſection upon metallic ſolutions, he has confined himſelf to oppoſe to the antiphlogiſtic doctrine a ſeries of queſ-

queſtions, which are equally embarraſſing on every hypotheſis, the ſolution of which appears to depend upon a concurrence of affinities not yet proved, which offer, in a word, matter for new reſearches, but are not, for that reaſon, real objections.

Nevertheleſs, the known facts already prove, that in the circumſtances here ſpoken of, the inflammable gas really comes from the water.

1. This is proved by the calcination by the vapour of water, where the increaſe of weight of the metallic oxide cannot come but from one of the principles of the water, becauſe the air has no acceſs to it. If it be aſſerted that the water itſelf then becomes fixed in the metal, we muſt admit two kinds of calcination, without any ground for ſo doing; for there is not really any difference between iron oxided in this operation and iron burned in vital air. Indeed the author inſiſts, ſec. 9. page 166, upon the difference between the iron thus oxided by water, and ruſt formed in the air; but this laſt is in the ſame ſituation as all other metallic oxides, which in proceſs of time become charged with carbonic acid; now this carbonic acid is not eſſential to their ſtate as oxides.

Moreover, Mr. Kirwan in the ſame ſection, page 177, formally excludes this difference of calcination by water or by air, ſince in ſpeaking of the experiment of Dr. Prieſtley, which

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we have quoted in our reply to the ſecond argument, he explains the increaſe of weight of iron burned in vital air, by affirming that this air firſt united to the phlogiſton of the iron, with which it formed water, and that this water was abſorbed by the iron. Mr. Prieſtley poſitively aſſerts, vol. 6. page 77, that he found by various proofs, that it is a pure calx of iron or ſcoria, abſolutely ſimilar to the ſcales of iron burned in the open air, and to that which he calls finery cinder.

Laſtly, this opinion of the abſorption of water itſelf by iron, which was propoſed by Mr. Cavendiſh, did not, doubtleſs, appear to him ſufficiently well eſtabliſhed to maintain the cauſe of phlogiſton, as he has ſince abandoned it.

2. It is equally certain, that the hydrogenous gas, which is diſengaged during metallic ſolutions in acids, comes from the water and not from the metal.

Theſe ſolutions preſent two very different caſes, as the author himſelf acknowledges, ſection 10. One where the acid is partly decompoſed, and then there is no production of hydrogenous gas; this happens with the nitric acid, and with the concentrated ſulphuric acid; the other wherein no part of the acid is decompoſed, and then a quantity of hydrogenous gas is obtained; which takes place with the diluted ſulphuric acid, the muriatic acid, &c.

&c. But in both caſes the metal aſſumes the ſame ſtate of oxide, acquires the ſame properties, and the ſame augmentation of weight, whence it invincibly follows, that the ſame principle was employed in the one as well as in the other caſe, to form the ſame compound. Now ſince in the firſt caſe it received a portion of vital air from the acid, it is neceſſary in the ſecond, that this principle ſhould have been furniſhed by ſome other ſubſtance; and ſince there was only water in contact with it, Mr. De la Place had reaſon to think that it was the water which afforded this portion. It is not ſurprizing, then, that hydrogenous gas ſhould be diſengaged, and that it ſhould not be diſengaged but in this caſe; it is a neceſſary conſequence of the decompoſition of water, a conſequence of this firſt truth; and completes in the moſt ſatisfactory manner the explanation of the two contrary phenomena.

We apprehend, therefore, that we may conclude, from the examination we have made of theſe arguments, that there is no proof ariſing from them of the exiſtence of phlogiſton; no proof of its identity with inflammable gas; nor even any induction capable of ſhewing that combuſtibles and metals are compounded bodies before combuſtion and calcination; in a word, that all the phenomena are explained in a much more ſimple

and

and certain manner, without any hypotheſis, by attending only to the ſubſtances, which manifeſt themſelves by ſenſible effects, and whoſe exact weight can be found in the calculation of the products; which is the only ſolid baſe of an analyſis.

The End of the Notes of the French Academicians.

REMARKS

REMARKS

UPON THE

ANNOTATIONS

OF THE

FRENCH ACADEMICIANS,

BY

Mr. KIRWAN.

Remark on Page 10.

I Cannot perceive in what reſpect I have failed in giving a true idea of Mr. Lavoiſier's theory, except that I have omitted the diſtinction he makes between dephlogiſticated air and its baſis, the other conſtituent part being elementary fire; but in the ſummary expoſition, given in the introduction, I thought ſuch a diſtinction needleſs, and ſo much the more as it means no more than the difference between dephlogiſticated air in an elaſtic and in a concrete ſtate; a diſtinction in which we both agree. In the ſecond ſection I particularly mention it in his own terms.

Page

Page 19. line 14.

I never formed any hypotheſis to explain the conſtitution of either inflammable or dephlogiſticated air, but always looked upon them (relatively to the preſent ſtate of our knowledge) as ſimple ſubſtances, in the ſame manner as they are conſidered by the antiphlogiſtians themſelves.

Page 21. line 16.

TO call dephlogiſticated air the principle of inflammability, is only a play upon words; Mr. Lavoiſier well knows that the ſpecies of air he himſelf, in his table of affinities, calls the principle of inflammability, is that which I and every one elſe has hitherto diſtinguiſhed by the name of inflammable air. Dr. Crawford has lately ſhewn that it contains far a greater quantity of fire and light than dephlogiſticated air does, namely in the proportion of 21 to 4.

Page 55. laſt paragraph.

THE imperfections to which Mr. Lavoiſier acknowledged his table of affinities to be liable, are only thoſe general defects which are found in all the tables hitherto publiſhed, but thoſe I have made to this table are found in it only, and are the natural reſult of the fallacy of his peculiar ſyſtem; and hence I could

could not give notice to the reader that he made them, as in fact he entirely overlooked them. The common tables, though in ſome reſpects faulty, as I mentioned on another occaſion, yet have been the inſtruments of the moſt important diſcoveries, as may eaſily be ſeen in peruſing the works of the immortal Scheele.

I think it very fair to argue againſt any ſyſtem by ſhewing it to be contradictory to its own principles, or that theſe principles are inconſiſtent with eſtabliſhed facts.

Page 61.

THE principle here laid down by Mr. Lavoiſier is very juſt; it is only its application which is conteſted. It is as certain that metals are formed of a peculiar calx and inflammable air, as that water is formed of dephlogiſticated and inflammable air, it is alſo certain that inflammable air has been ſeparated from ſome metals where no water was ſenſibly preſent, but there is no clear inſtance of the ſeparation of inflammable air from water. When any ambiguity ariſes about the origin of a principle, the only remedy we have is to try each opinion by its conſequences, as Mr. Bergman has laid down in his treatiſe *de indagando vero*, letter *B*. In this caſe the opinion that aſcribes the origin of inflammable air to the decompoſition of water introduces univerſal confuſion, and is inconſiſtent

conſiſtent with the principles even of thoſe that ſuppoſe it, as we have already ſeen.

Page 71. the only point which divides us.

IT is very true that I do not content myſelf with the immediate inferences from *ſingle* facts. In my opinion, the book of nature ſhould be interpreted like other books, the ſenſe of which muſt be collected not from ſingle detached paſſages, but from an attentive conſideration of the whole, ſo that what is defective in one text may be ſupplied from another. On the preſent occaſion, my opinion of the formation of the vitriolic acid is not exactly ſtated. I do not think that undecompoſed ſulphur exiſts in this acid; on the contrary, I think the inflammable principle is immediately united to the concrete dephlogiſticated air, and not to the baſis of ſulphur.

That this principle exiſted in ſulphur before decompoſition, I have already proved; and I do not think theſe proofs invalidated by any thing here alledged.

Page 83. line 6.

THE original words, *As to the acid depoſited*, are rendered by *quant a l'acide nitreux*, in the French tranſlation.

Page 83. line 25.

THE original words, *The inflammable air was taken up partly by the metal which it revived, and partly by the decompoſed nitrous acid, &c.* are rendered by *dans ce cas une partie du*

gas

gas inflammable a été absorbée par le métal qui se revivifie, l'autre partie est décomposée par l'acide nitreux, &c.

Page 98. line 18.

THERE is a mistake in the original, it should be 59,8 grs.

Page 116.

IF I had given no other proof of the existence of the inflammable principle in sulphur, but that with the nitrous acid it affords nitrous air, and had given no other proof of the existence of this principle in nitrous air, but that it dephlogisticates sulphur, this undoubtedly would be a vicious circle. But let the impartial reader judge.

Page 118.

IN melted nitre the acid is phlogisticated, and being exposed to dephlogisticated or common air, it absorbs pure air, and thus regains that part of fixed air which it had lost.

Page 119.

THE explanation I gave is deduced from experiments; Mr. Berthollet avows he can only substitute vague solutions in its room.

Ibid.

THE existence of charcoal in any metal has never yet been proved.

Page 121.

Mr. Monge ſays he did find fixed air. Mem. Par. 1783. p. 85.

Page 122. line 21.

THE Memoirs of the Academy of Paris for 1785, were not publiſhed when my eſſay was printed, nor have I ſeen them as yet; but in my paper on hepatic air, it has been ſhewn that deacidified nitrous air commonly contains a portion of nitrous vapour.

Page 123.

Mr. Lichtenſtein has ſhewn that charcoal dephlogiſticates the common ſmoking ſpirit of nitre, and makes it paſs colourleſs when diſtilled over it. Dr. Prieſtley certainly employed the radical acid of vinegar in diſſolving the calcareous earth, and not common or diſtilled vinegar; but the antiphlogiſtic theory can derive no advantage from this circumſtance: on the contrary, it confirms us in the opinion of its falſehood; for Mr. Berthollet muſt own that pure dephlogiſticated air has never been made to unite to calcareous earths, therefore this air muſt have been in the ſtate of fixed air when it united to this earth. Thus this experiment fully confirms my theory of fixed air.

I had no occaſion to quote other experiments

ments made by Dr. Prieſtley on calcareous ſtones: the quantity of impure air he received from ſome of them, appeared to me to proceed from the tranſmiſſion of the external air through the pores of his retorts, as happened when he diſtilled water; but theſe experiments had no relation to the matter I treated of, for dephlogiſticated air is never procured in that manner, and Mr. Berthollet allows it can be procured from acetous ſelenite, made with the radical acid of vinegar.

What Mr. Berthollet adds concerning experiments made without any diſtinct view, is not at all applicable to thoſe I have quoted from Dr. Prieſtley's works. This able philoſopher had a conſtant view to the ſpecies of air each ſubſtance afforded, and if in the immenſe number he has made (more than all the experimenters of Europe taken together) he has been miſtaken three or four times, in attributing the products to ſubſtances to which they did not belong, he has been generally the firſt to rectify publicly his miſtake, or correct it if detected by any one elſe. It is from a multitude of experiments, not made with a view of ſupporting any ſyſtem, but fully and impartially ſtated, and not by wire-drawing one or two, and forcing them into the ſupport of a general ſyſtem, that nature is to be interpreted.

Page 134.

WHEN the dephlogiſticated marine acid is

converted into common marine acid by the action of light, the phlogiſton unites to the baſis and quits the fixed air, which then becomes dephlogiſticated air; but it cannot be ſaid that the marine acid communicated nothing to the manganeſe, as the quantity and proportion of the ingredients are very different; the fixed air, when decompoſed, reſtores to the marine baſis the phlogiſton this latter had given to the manganeſe.

Page 138.

THERE are ſeveral errors in the French tranſlation, which make my theory of aqua regia unintelligible.

Page 141.

AS Mr. Berthollet's Memoir on the dephlogiſticated marine acid, was not printed when my eſſay on phlogiſton was publiſhed, I could give no other account of his opinion than that which I tranſcribed from his own extract of that Memoir, and in his own words. Neither have I as yet ſeen that Memoir, and therefore am at a loſs how to ſtate his opinion.

Page 161.

THESE queſtions are very eaſily anſwered: by means of a double affinity, the dephlogiſticated air in the nitrous acid, attacking part of the phlogiſton of the ſugar, the nitrous baſis

another

another part, while the baſis of the ſugar acquires the newly formed fixed air in addition to that it already poſſeſſed. An acid of ſugar is alſo formed by diſtillation, with properties ſomewhat different from that formed by the nitrous acid. Laſtly, the aerial acid is demonſtrated in the oxalic acid, as he calls it, for it affords this air by diſtillation; and if we cannot recompoſe this acid out of its aſſumed principles, neither can the partizans of the new opinion recompoſe it out of theirs.

Page 162.

HERE Mr. Fourcroy ſeems to allow that I have ſufficiently refuted the antiphlogiſtic theory of this acid, ſuch as it appeared in print at the time I wrote my eſſay. The ſubſequent alterations or improvements I have not yet ſeen; but, from the ſpecimen here given, they appear to me as ungrounded as the original theory.

Page 170. After the firſt paragraph of Mr. De la Place's Note.

THE anſwer is ſo eaſy on my principles, that it ſuggeſts itſelf. A metal is calcined merely by the loſs of its phlogiſton, though it generally unites at the ſame time to another ſubſtance, but it is not the union with another ſubſtance that conſtitutes calcination; thus the calces of lead may be deprived of a

great part of the air that unites to them, and ſtill remain calcined for the greater part. When iron is calcined by the dilute vitriolic acid, the acid is not decompoſed, but the phlogiſton is ſeparated from the iron, nor is there any proof that water is decompoſed, or that the iron unites to the oxigenous principle. The remaining objections of Mr. de la Place have been already obviated.

Page 193. After Mr. Monge's Note.

THE Memoir which Mr. Monge read to the Academy in 1781, is not printed among thoſe of that nor of any ſubſequent year to 1784 incluſive; I cannot therefore comment upon it. I ſtill adhere to my own explanation, and leave the reader to decide.

Page 207.

THE order I have followed appeared to me the moſt natural: firſt, expoſing the different opinions held on this ſubject; then eſtabliſhing my own, and refuting the opinion of the antiphlogiſtians, with reſpect to the decompoſition of water, and the nature of charcoal; and laſtly, ſupporting my own opinion, concerning the formation of fixed air, and its decompoſition.

Page 214. line 24.

I uſed the ſame expreſſion as Dr. Prieſtley himſelf.

Page

Page 218. line 23.

UPON this whole paragraph I need only remark, 1. That water expels more inflammable air from iron than is expelled during its ſolution in acids, as Dr. Prieſtley remarks, and therefore that, contrary to the aſſertion of our author, water reduces iron to a perfect calx. 2. That he allows that the calx of iron afforded by water gives no inflammable air by ſolution in acids, which it certainly would if not thoroughly dephlogiſticated. 3. That he allows it diſſolves in acids with ſcarce any efferveſcence, and therefore does not contain his oxigenous principle, if the acids be not altered, which he does not pretend.

Page 223. After Mr. Berthollet's Note.

I acknowledge that during the evaporation of my calx of lead, the calx might have abſorbed ſome air. Mr. Gren's authority is equally adverſe to the antiphlogiſtians; he refutes Mr. Lavoiſier's ſyſtem with equal zeal as every other, but that which he ſubſtitutes in their room is that which Mr. Morveau had formerly adopted long before the modern diſcoveries on air, and has long ſince rejected, namely the abſolute levity of phlogiſton.

Page 234. line 22.

HERE I cannot refrain from expreſſing my

admiration of the intereſting diſcovery made by Mr. Morveau, of the origin of the volatile alkali obſerved in the nitrous ſolution of tin.

Page 240.

I paſs over the ingenious anſwers of Mr. Fourcroy to the nine firſt queſtions; the chymical reader need only compare them with the explanation given by Mr. Bergman, Scheele, and my own, and decide which is the moſt ſatisfactory. But as to the inflammable air which Mr. Fourcroy intimates he diſcovered in alkaline hepatic air, I muſt beg leave to doubt, until I ſee his proofs.

Page 257.

I leave the candid reader to judge of the validity of Mr. Lavoiſier's explanation; but I muſt obſerve that the experiments to which he does not deign to anſwer, are neither equivocal nor uncertain, being made by chymiſts of reputation, and particularly by Mr. Bergman, and moſt of them repeated by myſelf.

Page 277. At the end.

THE experiment alluded to was made by Mr. Rinman, the moſt experienced iron maſter perhaps in Europe. That the heat was ſufficiently great is evident, for other pieces of iron not contained in the glaſs, but in the

ſame

ſame box, were converted into ſteel. See Rinman, § 73. xix.

Page 291. After the ſecond line.

THAT combuſtion ariſes from the union of dephlogiſticated air to ſome other ſubſtance, is allowed in both ſyſtems. In my opinion it unites in all ſorts of combuſtion to inflammable air, becauſe I ſee it evidently and confeſſedly does ſo in ſome caſes, and no adequate reaſon has been adduced to ſuſpect that, in any caſe, it unites to any other ſubſtance. Mr. Morveau thinks that the difference of reſiduums left after the combuſtion of inflammable air and ſulphur, indicates a difference betwixt the ſubſtances to which dephlogiſticated air unites; but I think this reaſon inſufficient, for the inflammation of wood, and that of the ſpirit of wine, leave very different reſiduums, and yet both confeſſedly ariſe from the union of dephlogiſticated and inflammable air. Again, Mr. Morveau objects that by the ſame mode of reaſoning the vitriolic and marine acids might be proved to be one and the ſame, as they both agree in diſſolving the mineral alkali; and certainly the inference would be natural, if it could not be proved that the vitriolic acid did not exiſt in the marine, or that the marine did not exiſt in the vitriolic acid; but the proofs that neither of them contain the other are ſufficiently clear.

clear. On the other hand, it has never been proved that ſulphur or metals did not contain inflammable air; on the contrary, their agreement, not only in reſpect of inflammability, but in various other reſpects with bodies that confeſſedly contain that air, is a ſufficient inducement, according to the ſtricteſt rules of philoſophic reaſoning, to believe that they do contain the inflammable principle.

Page 294. line 17.

HERE the annotator conſtantly ſuppoſes that dephlogiſticated air can unite to various ſubſtances, a quality peculiar to acids, among which this air cannot pretend to be claſſed. That the detonation of nitre with metallic bodies does not depend on the affinity of the dephlogiſticated air of the nitrous acid with thoſe bodies, but ſingly on the affinity of that air with the phlogiſton of thoſe bodies, may be deduced from the principles of the antiphlogiſtians themſelves. For according to theſe, ſilver and copper, being ſoluble in the nitrous acid, have the power of decompoſing that acid, and uniting to its vital air; yet ſilver will not detonate in the leaſt, and copper very little with nitre, therefore on their own principles detonation does not proceed from the union of vital air with the metals *in toto*.

I think I have at leaſt as good a right to ſuppoſe

ſuppoſe phlogiſton, or inflammable air, preſent in every caſe of inflammation, as the antiphlogiſtians have to ſuppoſe charcoal preſent in every caſe where fixed air is produced; and if my principle be denominated hypothetical, becauſe I cannot in all caſes exhibit it, though its exiſtence be in every caſe grounded on the cloſeſt analogies, much more may theirs, which is founded on no analogy at all, but on this ſingle experiment, that *vital air and charcoal afford fixed air*; for hence they boldly infer, that *wherever fixed air is produced, charcoal exiſts:* hence they ſuppoſe its exiſtence in ſpirit of wine, ether, and the acid of ſugar, in none of which the ſmalleſt trace of it can be found; nor have they ſeparated it from vital air, no more than I have ſeparated inflammable air from ſulphur, in which, upon good grounds, I ſuppoſe it to exiſt. That their charcoal is a more hypothetical entity, appears from this, that they have aſſigned it no part in any ſubſtance whatſoever, but merely that of affording fixed air in all caſes where this is produced, by the hypothetical decompoſition of water, when they can no otherwiſe find vital air to unite with it.

As to Dr. Prieſtley's experiments, it is plain they are no way adverſe to my opinions, as he not only agrees with me in the general doctrine of phlogiſton, but alſo in that of the production of fixed air, and lately confirmed it by the moſt ſatisfactory experiments. In the experi-

experiment quoted by Mr. Morveau, water and not fixed air was chiefly formed as a red heat was applied. The proportion and condenſation of the ingredients of water and fixed air, are not the ſame as I have already mentioned, and therefore they conſtitute compounds, whoſe properties are eſſentially different. I never ſaid that fixed air might be converted into water, and need no ſuch hypotheſis. The baſis of the nitrous acid is again a quite different compound, and I have ſhewn in the 8th ſection, how different compounds may be formed of the ſame ſubſtances, and in this the antiphlogiſtians themſelves agree with me.

Page 296.

IT is not by accumulating ſuppoſitions, but by the knowledge collected from numerous different experiments, that the internal and inviſible action of bodies on each other is explained. The quantity of phoſphorus acidified, is always proportioned to the quantity of fixed air abſorbed, as this is to the quantity of phlogiſton ſeparated.

Page 297. laſt paragraph.

Mr. Morveau will find no contradiction in this caſe, when he conſiders that both the ſlagg and finery cinders were formed in a red heat, and conſequently abſorbed water.

Page 299.

HERE Mr. Morveau uſes the ſame mode of reaſoning, with reſpect to calcination, that I uſed with reſpect to inflammation; he thinks that calcination cannot be produced but through the intervention of vital air, as I think that inflammation neceſſarily requires inflammable air. If he did not find my mode of reaſoning ſatisfactory, though founded on numerous analogies, and in ſome caſes on direct experiment, much leſs can I adopt his, which is founded on ſimple conjecture, and contradicted even by the antiphlogiſtic table of affinities.

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Government of Maharashtra
on 25 June, 2016